

OPTICAL STORAGE EFFECTS IN GaP

by

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Introduction

Successful exploitations of optoelectronic devices in the last few years have increased the demand for more information on optical properties of semiconductors. Photocells are used for the power supply in satellites and may also be important in converting solar energy on earth. Light emitting diodes (LEDs) which are found to be extremely reliable components, are already wide-spread in alphanumeric displays for pocket calculators, cars, etc. and have considerably promoted man-machine communication. They will also be important parts of integrated optics which is a growing new field related to telecommunications, information processing in computers etc. in which several other optical effects of semiconductors will be employed.

GaP is a large bandgap semiconductor material (2.25 eV at room temperature), which as implied in the earlier papers constituting this thesis, was difficult to obtain because of a rather complex technology for production and sample preparation. Because of proven suitable properties for LEDs in the visual range, GaP of good quality has recently become commercially obtainable and various preparation processes are being developed. This gives an indication of the rate of development in this narrow part of the semiconductor science.

The Author's Contribution

There have been two objectives for the investigations presented here. One is to add some information on extrinsic properties of a large bandgap material and the other is to study some effects in GaP devices with potential application possibilities.

The extrinsic properties dealt with concern the behaviour of energy levels in the forbidden bandgap lying deep enough so that thermal excitation could be neglected. Theoretical models are deduced for properties related to optically induced charge exchange between such deep energy levels themselves or between them and the conduction band or the valence band. Usually it is difficult to study such interactions experimentally because of the screening of the unavoidable shallow levels. The experimental requirements were found to be fulfilled, however, by impurity levels in GaP which is the reason why the experiments were concentrated on GaP. Experimental methods using charge accumulation instead of current measurements were also developed to obtain higher resolution on required data.

The new effects obtained by optically charge exchange or accumulation of optically excited charge carriers in the samples used have initiated a study of applicability where several suggestions are made.

The thesis consists of the introduction and summary above and the following four papers.

- I Storage effects in photoconducting GaP-Cu
phys stat sol 28, 547 (68).
- II Charge-carrier capture and its effect on transition capacitance in GaP-Cu diodes J Appl Phys 40, 2526 (69).
- III Semiconductor element with charge storage effect.
Patent application 314.073 USA (331 864)
- IV Investigation of optical properties of a GaP MIS-structure.
Preprint.

Papers I-III in cooperation with H. G. Grimmeiss.

The first paper describes how charge storage can be obtained by excitation with intrinsic and extrinsic light in photoconducting GaP-Cu. Although conditions on the material for obtaining this are extreme, the related effects were stable enough for several experiments to be done. Correlation between the supralinear photoconductivity and optical charge exchange is shown. The remaining charge exchange in darkness after the "pumping" light is off makes the sample sensitive to infrared light. The binding energies of the impurity levels involved were estimated to be between 0,6-0,8 eV and at least one of them is suggested to be a Cu-level.

The promising results from the above investigation on charge storage in homogeneous material free of any space charge stimulated the continued research. To facilitate the experiments, however, a more easily obtainable and controllable device than the high ohmic photoconducting sample used in Paper I was desired. A device with a space charge layer is suggested. The conditions of very few free charge carriers and a Fermi level almost in the middle of the bandgap are thus almost automatically fulfilled.

In the second paper, charge exchange is optically and electrically induced in the space charge layer of a pn-junction in GaP-Cu. Experimental methods based on measurements of the transition capacitance of the pn-junction were found to give sensitive measurements, and a theoretical model deduced for charge exchange between two deep levels in the space charge layer and the influence on the CV-curve were supported.

The decay of the induced charge exchange was very slow in darkness and also at room temperature, and the related increase of the capacitance was almost constant for several hours.

Considerable charge storage which could be released rather fast was possible. This reverse charge exchange was obtained by light of energy less than half the bandgap. The related transient photo-effect was found valuable in studying some properties of the energy levels involved.

Some of the properties of the easily made samples for the experiments described in Paper II seemed to be useful in different applications and in Paper III, a semiconductor element is described which based upon optically and electrically induced charge exchange and the reverse process can be used for a plurality of applications such as light detection, light integration, optical memory storage and capacitance variation.

In the investigations of optical properties of GaP metal-insulator-semiconductor (MIS) structures presented in Paper IV, the two earlier mentioned objectives are combined. The process of making an MIS-structure may not affect the bulk material very much. Also it was of interest to see if deep-lying impurity levels in commercially available material which was not intentionally doped could be studied by methods related to the earlier developed. The growing interest in charge-coupled devices (CCD) made in silicon also promoted the research on optical properties of MIS-structures in large bandgap material with potential applicability.

This method was based on a principle using excess charge, due to light excitation in the space charge region which is accumulated at the semiconductor-insulator interface. An experimental method was developed to study properties of deep lying impurity levels. Because of the large bandgap and a low generation in the depletion region, the light-induced effects were almost in steady state which indicated that such MIS-structures also may be useful in applications mentioned in Paper III.

Acknowledgements

I am greatly indebted to Professor H. G. Grimmeiss for continuous support, interest, and encouragement.

I also want to acknowledge all members of the department of Solid State Physics for the stimulating atmosphere and the scientific interaction.

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Storage Effects in Photoconducting GaP-Cu

By

H. G. GRIMMEISS and G. OLOFSSON

Experimental evidence is given that charge storage exists in photoconducting GaP-Cu after excitation with both intrinsic and extrinsic light. Appreciable storage is still observed one hour after excitation even at room temperature. Measurements of stored charge as a function of ir photon energy, external voltage, and excitation density confirm that such effects as supralinear photoconductivity, etc., are governed by optical charge exchange in agreement with previous investigations.

Es wird experimentell gezeigt, daß in photoleitendem GaP-Cu nach der Anregung mit Licht größerer oder kleinerer Energie als die Bandkante eine Ladungsspeicherung auftreten kann. Eine beträchtliche Speicherung ist eine Stunde nach der Anregung selbst bei Zimmertemperatur noch nachzuweisen. Die gespeicherte Ladungsmenge wurde in Abhängigkeit von der IR-Photonenenergie, äußerer Spannung und Anregungsdichte gemessen. Die erhaltenen Ergebnisse bestätigen in Übereinstimmung mit früheren Messungen, daß Effekte wie superlineare Photoleitung usw. durch einen optischen Ladungsaustausch bestimmt werden.

1. Introduction

Copper doping has been shown to provide a remarkable photosensitivity in GaP in both the visible and ir regions of the spectrum [1 to 5]. Under certain circumstances, a supralinear dependence of the photoconductivity on excitation density and a strong ir quenching of the photoconductivity have been observed [3]. These effects have been attributed [3] to optical charge exchange and Bowman [6] has given additional evidence for this explanation by photo-Hall measurements. In this paper, we will report and discuss several experiments carried out to obtain further information on the optical charge exchange mechanism [7] in Cu-doped GaP, since we believe that this mechanism is also responsible for some other interesting effects.

Using the same type of material as in [3], we have obtained evidence suggesting that in our samples at least two types of centres are involved in the charge exchange: acceptor levels "a" having low electron-capture cross-sections and deep-lying donor centres "k" having high electron-capture cross-sections. The acceptor centres are present after doping the sample with Cu, while the origin of the donor centres is unknown.¹⁾ We assume that the donor centres act as recombination centres and that the Fermi level lies between the acceptor and donor levels in our high-ohmic samples. The supralinearity of photoconductivity in highly-compensated material has thus been explained [3] as originating from the filling-up of donor centres by electrons from the occupied acceptor centres (due to hole capture at the acceptor centres). The ir quenching of the photo-

¹⁾ ESR investigations indicate, however, that the donor centres may originate from Fe.

conductivity is the reverse of this process, namely the emptying of filled donor centres by means of free holes created by ir ionisation of unoccupied acceptor levels. Therefore appreciable ir quenching is only observed after the onset of supralinear photoconductivity [3]. From this explanation, it should be expected that those electrons which occupy donor centres by excitation from the acceptor centres should remain in the donor centres even after the source of excitation is removed when no direct recombination between charge carriers in the acceptor and donor levels is possible and both types of centres are assumed to have large binding energies i.e. thermal release can be neglected. In the next chapter we give experimental evidence that charge storage indeed occurs and that appreciable storage is still observed one hour after excitation even at room temperature.

2. Experimental Observations and Discussion

From previous investigations [1, 3, 5], it is known that electrons can be excited from the valence band into the acceptor levels by optical means, if not all of these levels are occupied by electrons. This process gives rise to an ir sensitive photoconductivity in (weakly) p-type GaP-Cu. In our n-type material, no change in conductivity is observed if the samples are illuminated only with ir light. These results offer a possibility of investigating the storage effects mentioned above. We therefore selected a highly compensated sample with the Fermi level lying just beneath the donor levels. For low voltages, the change of conductivity with ir illumination could be neglected, because nearly all acceptor levels were occupied with electrons. On the other hand, in thermal equilibrium many of the donor levels were empty. It was therefore possible to fill these donor centres with electrons from the acceptor centres by illuminating the sample, e.g. with intrinsic light (5000 Å) of reasonable intensity. At the same time the acceptor centres were emptied. If this situation remained even after irradiation, the concentration of empty acceptor levels and filled donor levels in darkness should have increased considerably. Consequently, the sample should now show a change in conductivity when illuminated with ir light alone because free holes can then be created by the ir light, due to ionisation of the empty acceptor levels. When all the acceptor levels are filled by this process, the supply of free holes ceases and hence the change in conductivity due to the recombination of free holes with electrons from the donor levels. To prove this, the sample was first illuminated with ir light and then kept in darkness for some time. After being biased with a p.d. of 4 V, it was again illuminated with ir light (0.97 eV) for a time $t_s = 0.5$ s. Little change in conductivity could be observed (Fig. 1, above). The sample was then illuminated with intrinsic light (2.5 eV) for a time $t_p = 15$ s, kept in darkness for a time $t_w = 15$ s and again illuminated with ir light (0.97 eV). This time a transient increase σ_{st} in conductivity was clearly observed (Fig. 1, below).

Such a pronounced storage effect can only be observed when the material is properly compensated. If the Fermi level is situated too low, the above-mentioned ir photosensitivity masks any storage effect present. If the Fermi level lies too high, many of the k-levels are already occupied in thermal equilibrium and no appreciable optical charge exchange can be achieved. Furthermore, in less compensated samples the dark current can also give rise to difficulties. From seven samples with different degrees of compensation which all showed



Fig. 1. Change in conductivity due to illumination with ir light ($1.2\ \mu\text{m}$) before (above) and after pumping. Vertical scale: $1.7\ \text{nA/div.}$, horizontal scale: $0.1\ \text{s/div.}$; $t_p = 15\ \text{s}$, $t_w = 15\ \text{s}$, $U = 4\ \text{V}$ (see text)

a more or less pronounced storage effect, we therefore selected one sample with the most suitable properties for our measurements. The sample had two alloyed Sn-contacts and a dark resistivity of about $10^{10}\ \Omega\text{cm}$. Below $400\ \text{V}$ essentially no rectification could be observed and the photovoltaic effects neglected. The results on the storage effect obtained were not changed when the sample was short-circuited during the pumping time t_p and/or during the waiting time t_w .

The time-dependence of the transient increase σ_{st} in conductivity is strongly influenced by the intensity of the ir light (Fig. 2), but the charge Q carried by this induced photocurrent is independent of the ir intensity. The charge Q induced in the sample by optical charge exchange has been measured using an

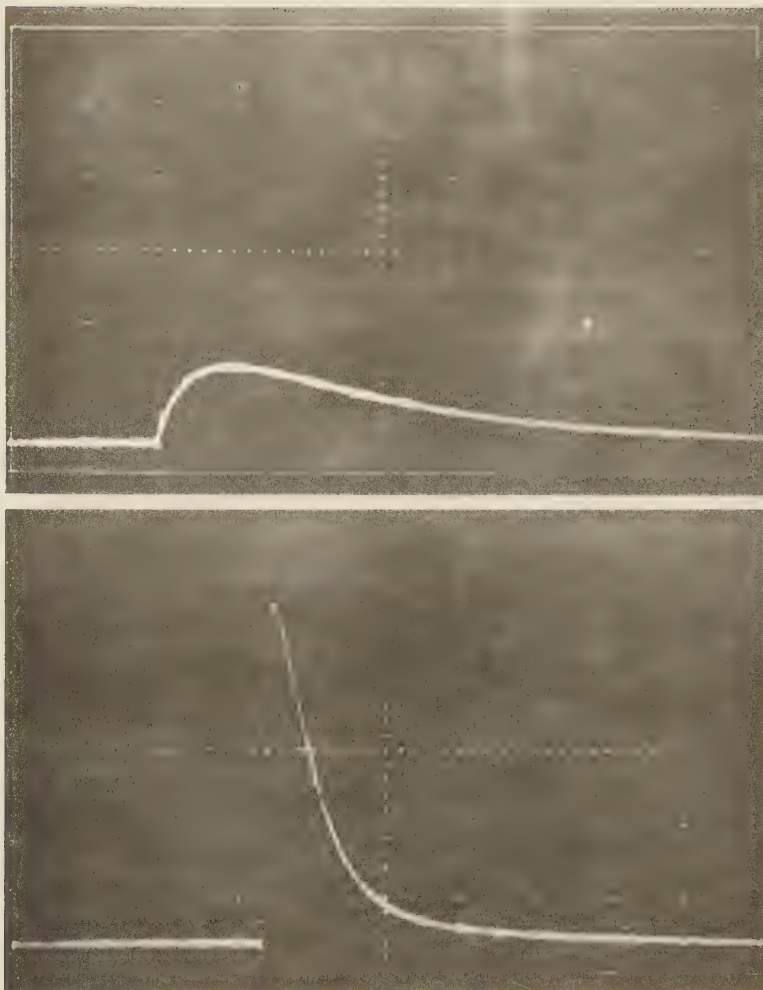


Fig. 2. Change in conductivity due to illumination with two different intensities of ir light after pumping. Upper curve with lower intensity. Vertical scale: 1 nA/div., horizontal scale: 0.2 s/div.; $t_p = 15$ s, $t_w = 15$ s

operational amplifier and a storage oscilloscope.²⁾ At higher voltages, Q is defined as the difference of the charge liberated in the circuit by illuminating the sample with ir light both with and without preceding illumination with intrinsic light. A change in intensity of the ir light by nearly 2 orders of magnitude gave no indication of any change in Q , in agreement with our explanation that Q is primarily caused by ionising the unoccupied acceptors originating from optical charge exchange. After complete pumping, Q is a constant and independent of the rate of emptying.

It may be worthwhile mentioning that in GaP optical charge exchange can be produced not only at intrinsic but also at extrinsic light energies. However,

²⁾ Tektronix type 549.

Fig. 3. Photocurrent i_{ph} (●) and stored charge Q (+) as a function of excitation density I_0 (W/cm²), expressed in arbitrary units.

by this kind of excitation, not only free electrons but apparently also free holes are created by two-step processes [8]. It has been found by a variation of the extrinsic excitation densities that a supralinear increase of photoconductivity can also be achieved (Fig. 3). It is therefore not unreasonable that the excitation spectra for the storage effect are in correspondence with the spectral sensitivity of the extrinsic photovoltaic effect observed in GaP-Cu photocells [4]. The low-energy cut-off for the creation of optical charge exchange is consequently determined by the energy difference between the conduction band and the acceptor levels responsible for the two-step excitation process. This has not necessarily to be a Cu level. The use of extrinsic light for charge exchange has the advantage of more homogeneous excitation and avoids surface effects.

On the other hand, it must be expected that the lowest ir photon energy capable of causing a charge Q is given by the binding energy of the acceptors and must be the same as for ir quenching of the photoconductivity according to our explanation, because both processes are caused by the same type of excitation. A comparison between the "relative quenching" of the photoconductivity [3] (Fig. 4) and Q (Fig. 5) as a function of the photon energy of ir light shows excellent agreement. Both sensitivities start between 0.6 and 0.65 eV (see also Fig. 8 in [3]). It is interesting to note that the decay in sensitivity in Fig. 4 is much more abrupt for extrinsic than for intrinsic light. Although the spectral sensitivity of Q is more or less constant for photon energies larger than 0.85 eV, the time dependence of the transient conductivity increase σ_{tr} is rather

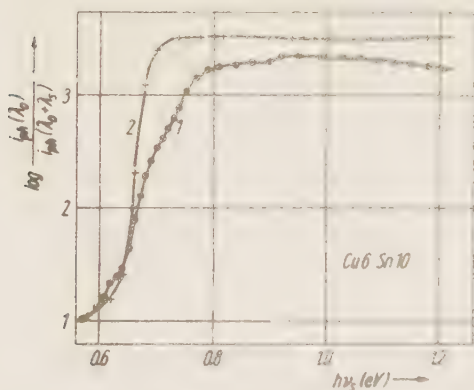
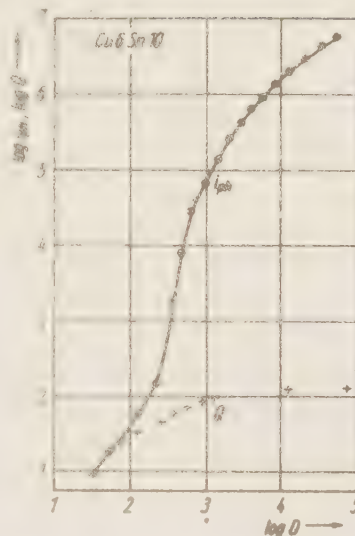


Fig. 4. Spectral distribution of "relative quenching" (see text). The exciting radiation, which caused constant intensity, has a wavelength of 5030 Å (curve 1) and 6360 Å (curve 2), respectively.

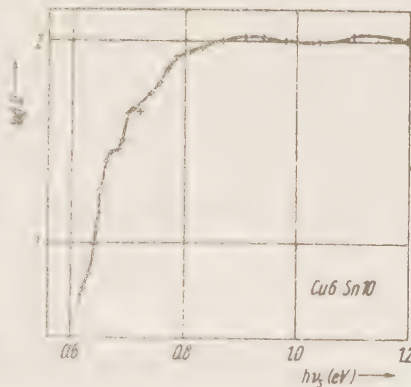


Fig. 5. Stored charge Q as a function of ir photon energy. $t_p = 15$ s, $t_w = 60$ s, $U = 4$ V.

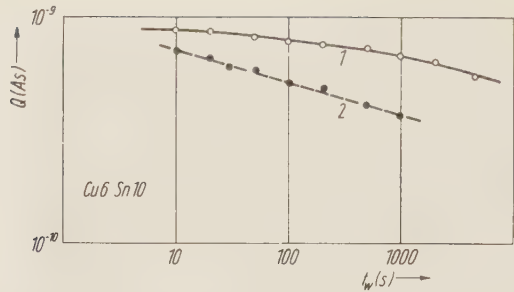


Fig. 6. Stored charge Q as a function of waiting time t_w . Curve 1: no external voltage during t_w ; curve 2: with external voltage during t_w . Pumping time $t_p = 15$ s

dependent on the photon energy. Typically the decay time of the storage peak (Fig. 1, below) decreases between 0.85 and 1 eV and increases for larger photon energies.

We have already mentioned that both centres involved in optical charge exchange are assumed to have large binding energies. This means that large storage times can be expected if the interactions between these two centres are small. In fact the decrease in Q with increasing waiting time t_w between pumping and ir illumination is rather small during the first hour if the sample is not biased during t_w (Fig. 6, curve 1). This apparently indicates that any interaction between these two levels is indeed small. A somewhat larger decrease in Q with increasing t_w could be observed if the sample was biased immediately after pumping, i.e. also during t_w . It has been found that the decrease in Q at constant t_w was continuous and depended on the fraction of time the sample was biased during t_w . This shows that the application of a voltage to the sample acts as a kind of de-ionisation of the optical charge exchange.

A similar behaviour could be observed when the charge Q was measured as a function of the applied voltage U . According to our explanation, Q can be expected to increase with external voltage U . If we assume a simple relationship

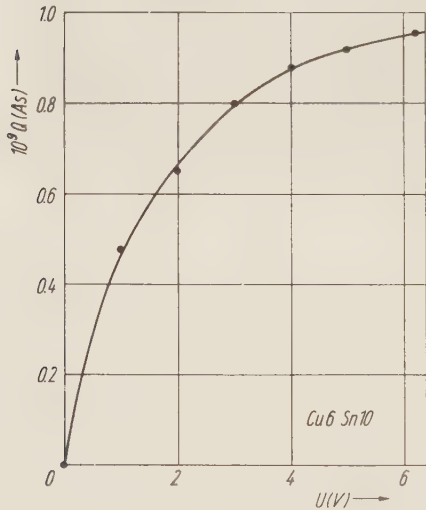


Fig. 7. Stored charge Q as a function of the external voltage U . $t_p = 15$ s, $t_w = 30$ s

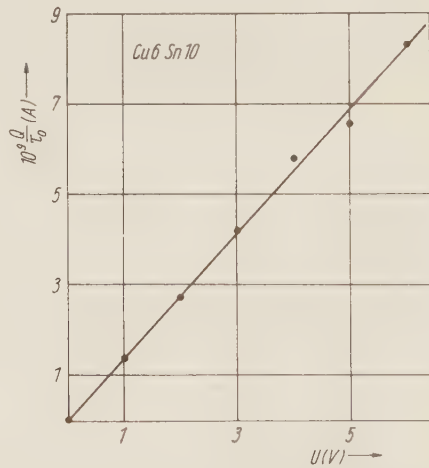


Fig. 8. Ratio of Q and decay time τ_0 of the transient photocurrent as a function of the external voltage U . $t_p = 15$ s, $t_w = 30$ s

such as $L_d = \mu \tau E$ between the drift-length L_d and the electric field E , then the dependence of L_d on E should be linear if the mobility μ and lifetime τ are assumed to be independent of E . A plot of Q against U (Fig. 7) showed no such linearity. If the electric field has really de-ionising properties, a simple linearity between L_d and E can no longer be expected because then a field-independent lifetime is rather unlikely. It has been found that the decay time τ_0 of the transient conductivity change σ_{st} decreases with increasing voltage U . Assuming the proportionality of τ_0 and τ , we have divided Q by the corresponding decay time and plotted Q/τ_0 against U (Fig. 8). The result is a straight line. Note that for $U = 0$, Q is zero. This was valid for all samples and indicates that we were not dealing with space-charge regions. In space-charge regions, we have found that storage currents can be achieved even without external voltages [9].

All these results can also be explained by the assumption that the donor levels are not recombination centres but traps with the same binding energies as the acceptor levels. One possibility of distinguishing between these possibilities is the determination of the type of free carriers created by ir light. So far such experiments have not yielded definite results with our sample because of experimental difficulties.

Another possibility for obtaining information about whether or not the donor levels are recombination centres is offered by the intensity dependence of the concentration of occupied recombination centres. Using a simple model, previous investigations have shown [3] that the number of occupied donor levels acting as recombination centres increases with the root of the excitation density until superlinearity is achieved. For higher excitation density the number of occupied donor levels is constant. If, therefore, the storage effect is caused by donor levels acting as recombination centres, the induced charge Q should vary with excitation density in the same way as the number of occupied donor levels. This has been found (Fig. 3). In these measurements Q has been determined with so long pumping times t_p that any further increase in t_p had no influence on Q . It is rather unlikely that the donor levels should show the same properties when acting as traps. Ryvkin [7], for example, found with Ge at low illumination intensity that the concentration of electrons in the donor centres acting as traps is independent of the intensity. Nevertheless further investigations are under way to clarify this question.

In agreement with previous experiments [4], additional measurements showed that at least two acceptor levels are present in GaP-Cu with binding energies of about 0.6 and 0.8 eV. As will be shown elsewhere, we have also reason to believe that each of the centres can be active in optical charge exchange depending on temperature and compensation. This might be the reason why the binding energy of the Cu level in GaP is given in the literature with different values. Whereas the 0.8 eV level is only observed in GaP-Cu, the 0.6 eV level has also been found in GaP with other dopings; it is therefore still an open question whether both levels are caused by Cu or not. Furthermore, it is not clear whether the acceptor levels are "pure" acceptors or complex.

3. Conclusion

The measurements of stored charges in photoconducting GaP-Cu as a function of time, ir photon energy, external voltage, and excitation density above described represent independent evidence that optical charge exchange is pos-

sible in this material, and further support the assumption that effects such as supralinear photoconductivity, etc., are governed by these processes.

Acknowledgement

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References

- [1] J. W. ALLEN and R. J. CHERRY, J. Phys. Chem. Solids **23**, 509 (1962).
- [2] D. N. NASLEDOV and S. V. SLOBODSHIKOV, Soviet Phys. — Solid State **4**, 2315 (1963).
- [3] H. G. GRIMMEISS and H. SCHOLZ, Philips Res. Rep. **20**, 107 (1965).
- [4] H. G. GRIMMEISS and H. SCHOLZ, Philips Res. Rep. **21**, 246 (1966).
- [5] B. GOLDSTEIN and S. S. PERLMAN, Phys. Rev. **148**, 715 (1966).
- [6] D. L. BOWMAN, J. appl. Phys. **38**, 568 (1967).
- [7] See, for instance, S. M. RYVKIN, Photoelectric Effects in Semiconductors, Consultants Bureau, New York 1964.
- [8] H. G. GRIMMEISS and H. KOELMANS, Philips Res. Rep. **15**, 290 (1960).
- [9] H. G. GRIMMEISS and G. OLOFSSON, to be published.

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Charge-Carrier Capture and Its Effect on Transition Capacitance in GaP-Cu Diodes*

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The induced photovoltaic effect and the change in transition-layer capacitance in alloyed GaP-Cu diodes have been investigated. Both effects can be explained by hole capturing in acceptor levels with large binding energy. The holes can be released by ir illumination which generates a transient shortcircuit current and quenches the change in capacitance. The spectral sensitivity of the transient photoeffect and of the capacity change is in agreement with other experimental results obtained in homogeneous material. Due to the large binding energy, thermal ionization of acceptor levels is very small at room temperature. Finally, the voltage dependence of the transition-layer capacitance is compared with theoretical considerations, taking into account not only deep lying acceptor levels but also donor levels with large binding energy.

I. INTRODUCTION

In recent years, several papers have been published on copper-doped GaP with respect to photoconductivity¹⁻⁵ and photovoltaic effects.^{4,6} These investigations indicated that high-resistivity GaP could easily be produced by copper diffusion and that these samples show large photoconductivity gains. Furthermore, it has been observed that the intensity dependence of the photoconductivity in high-resistivity GaP is often supralinear,^{3,5} and that the photoconductivity can be quenched rather effectively by ir light.³ Both effects have been explained³ by optical charge exchange⁷ between two impurity centers with large binding energies. At least one of these centers is probably caused by copper, namely the one that has a low electron-capture cross section and is responsible for the hole capture. These assumptions have been further supported by photo-Hall measurements⁵ and storage effects⁸ in homogeneous material. That hole capture can also play an important role in photovoltaic effects has been shown by the supralinear dependence of the short-circuit current on intensity in Cu-doped GaP diodes⁶ and by the spectral sensitivity of the photocapacitance of surface barrier junctions.^{4,9}

The purpose of this paper is to give direct support for capture of charge carriers in the transition layer of Cu-doped GaP diodes by investigating the induced photovoltaic effect. Furthermore, how these captured charge carriers affect the diode capacitance is discussed.

It is shown that a considerable concentration of holes can be stored in the transition layer and that due to the storage of holes, the transition-layer capacitance of the diode can be switched optically or electrically.

II. MATERIAL AND EXPERIMENTAL PROCEDURE

As starting material for the Cu-doped gallium phosphide samples, *n*-type GaP has been employed, made by causing gallium to react with phosphorous hydride. Copper has been incorporated into these samples by annealing them at 400°C in contact with metallic copper, as described in Ref. 3. Most of the resulting material had a resistivity between 1 and 10 $\Omega\cdot\text{cm}$ and was still *n* type. These *n*-type GaP-Cu samples have then been used for the fabrication of diodes by alloying.¹⁰ Because of the partial compensation of the copper-doped GaP, it is assumed that the positive space-charge region of the junction is much larger than the negative space-charge region.

Three main types of measurements are discussed, those of shortcircuit current (photovoltaic effect), capacitance and charge. Shortcircuit currents have been determined by measuring the voltage drop over a sufficiently small resistance in series with the diode. A Boonton capacitance bridge (type 75D) has been employed for capacitance measurements at 1 MHz. For frequencies below 1 MHz another transformer bridge built at the Institute has been used. Charges have been measured with an operational amplifier and a Tektronix storage oscilloscope type 549. The latter has also been used for the registration of transient effects. As light sources, either a Leiss monochromator or focused Reuter lamps in conjunction with interference filters have been used.

III. EXPERIMENTAL RESULTS

The current-voltage characteristic of the diode used for the investigations reported here is of the type as illustrated in Fig. 1 for diode B18 and discussed

* This work has been supported by the Swedish Council for Technical Research.

¹ J. W. Allen and R. J. Cherry, *J. Phys. Chem. Solids* **23**, 509 (1962).

² D. N. Nasledov and S. V. Slobodshikov, *Sov. Phys.—Solid State* **4**, 2315 (1963).

³ H. G. Grimmeiss and H. Scholz, *Philips Res. Reps.* **20**, 107 (1965).

⁴ B. Goldstein and S. S. Perlman, *Phys. Rev.* **148**, 715 (1966).

⁵ D. L. Bowman, *J. Appl. Phys.* **38**, 568 (1967).

⁶ H. G. Grimmeiss and H. Scholz, *Philips Res. Reps.* **21**, 246 (1966).

⁷ See, for instance, S. M. Ryvkin, *Photoelectric Effects in Semiconductors* (Consultants Bureau, New York, 1964).

⁸ H. G. Grimmeiss and G. Olofsson, *Phys. Status Solidi* **28**, 547 (1968).

⁹ Y. Furukawa, *Japan J. Appl. Phys.* **6**, 675 (1967).

¹⁰ H. G. Grimmeiss, W. Kischio, and H. Scholz, *Philips Techn. Rsch.* **10/11**, 386 (1963/64).

in Ref. 11 for GB 18. It is therefore assumed that the current through the diode is caused by recombination-generation processes in the space-charge region of the junction. The current in reverse direction at -2.5 V was less than 5×10^{-11} A at room temperature. No correlation, however, has been observed between the storage effect and the current-voltage characteristic of a diode. Diodes with completely different I-V characteristics can exhibit the same amount of storage effect.

In order to check whether a diode is exhibiting a storage effect or not, the following procedure was adopted using no external voltage sources: first the diode was illuminated with ir light only (1.2μ) for a time t_s and the current in the external circuit was registered as a function of time [Fig. 2(a)]. If the small peaks at the beginning and the end of the illumination are neglected, no appreciable current was observed and neither expected because the energy of the ir photons was too small even for a two-step excitation.¹² That nevertheless sometimes a photoeffect is observed also for photon energies $h\nu < \frac{1}{2}E_g$, is discussed elsewhere. When the diode then is illuminated with extrinsic (0.7μ) light (pumping) for a time t_p , the shortcircuit current increases rather slowly, and it takes considerable time before steady state is obtained [Fig. 2(b)]. If the diode is illuminated again with 0.7μ light, the steady state of the shortcircuit current is reached much faster [Fig. 2(c)]. Similar but less pronounced effects have also been observed by pumping with intrinsic light (0.5μ). After a fixed waiting time t_w in darkness (typically 15 sec), the diode was illuminated for a time t_s with ir light again. A transient shortcircuit current could now clearly be observed [Fig. 2(d)]. This transient shortcircuit current was not influenced by shortcircuiting the diode during the excitation with either intrinsic or extrinsic light and/or during the waiting time t_w . Furthermore, the charge Q represented by the transient shortcircuit current and defined as

$$Q = \int_{t_s}^{t_w} i_{sc}(t) dt$$

is not changed by varying the resistance in series with the diode between 10^2 and $10^6 \Omega$. This clearly shows that we are not dealing with high Ohmic photoeffects and that the storage effect is not caused by an ordinary capacity effect. Q values up to 10^{-8} A·sec have been observed in diodes that had an area of about 2×10^{-3} cm².

An explanation of the induced shortcircuit current can be given using the results obtained in homogeneous material.⁸ Because of the special geometry of the diode, electron-hole pairs are mostly created on the n side of the junction. This part of the diode, however, is to a

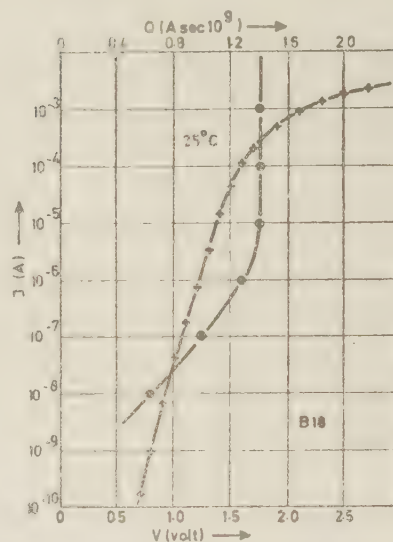


Fig. 1. Current-voltage characteristic of diode B 18. ●—● denotes the stored charge Q as a function of forward current.

certain degree compensated by deep lying acceptor levels (probably copper), having a large cross section with respect to free holes.^{3,6} This means that the free holes created during pumping and responsible for the shortcircuit current, are captured by the acceptor levels until most of the levels are empty. This corresponds to an increase in lifetime and the shortcircuit current is therefore increasing until steady state is obtained. After the source of excitation has been removed, the captured holes will stay in these levels at room temperature because of the high binding energy. This is the reason why repeated illumination exhibits a fast increase of the shortcircuit current when most of the acceptor levels are already empty. If the diode now is illuminated with ir light of sufficient energy to excite electrons from the valenceband into the empty acceptor levels, free holes are created that can take part in the shortcircuit current. Consequently, the smallest ir photon energy that can create holes for a transient shortcircuit current, should be determined by the binding energy of the acceptor level. Plotting Q as a function of the ir photon energy for constant t_p , t_w , t_s and excitation density (Fig. 3), a sensitivity edge is clearly observed at photon energies between 0.6 and 0.7 eV. This value is in good agreement with the corresponding curve for homogeneous GaP-Cu material,⁸ the "relative quenching" of photoconductivity³ and the ir stimulated and quenched photoeffect.⁶ Although Q is constant for ir photon energies larger than 0.75 eV, the decay time of the transient shortcircuit current depends considerably on the photon energy of the ir light (Fig. 4). As in homogeneous material, the decay time is shortest for light energies of about 1 eV and increases with smaller and larger photon energies. Due to the long decay time at low photon energies, the

¹¹ G. Bjorklund and H. G. Grimmeiss (unpublished).

¹² H. G. Grimmeiss, W. Kischio, and H. Koelmans, *Solid-State Electron.* 5, 155 (1962).

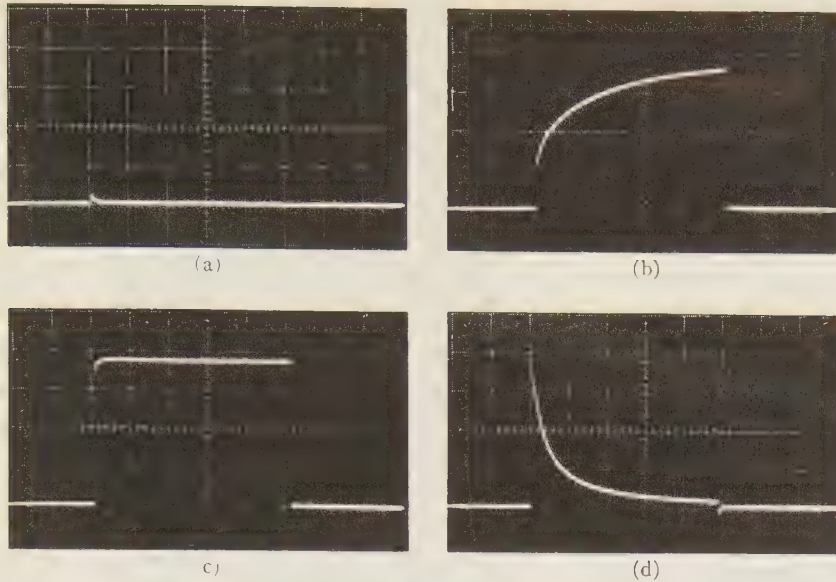


FIG. 2. Time dependence of the shortcircuit current i_{sc} for diode Q2 due to illumination with (a) ir light (1.2μ), when the diode has not been excited previously; (b) extrinsic light (0.7μ), when the diode has been illuminated with ir light (1.2μ) previously; (c) extrinsic light (0.7μ), when the diode has been illuminated with extrinsic light (0.7μ) previously; (d) ir light (1.2μ), when the diode has been illuminated with extrinsic light (0.7μ) previously. Vertical scales 5 nA/div ; horizontal scales 0.2 sec/div .

experimental difficulties for the determination of Q in Fig. 3 increase with decreasing photon energies. Nevertheless, it was clearly observed that there is no sensitivity for photon energies smaller than 0.55 eV . The constant Q value for ir photon energies larger than 0.75 eV , indicated that Q is mainly determined by acceptor levels with binding energies in a rather small energy range. The variation in decay time of the transient shortcircuit current with ir photon energy might therefore be caused by the valenceband structure.

From this explanation, it is clear that a faster rise-time of the shortcircuit current can be obtained with extrinsic light, directly after ir illumination, when hole capturing is made less likely. This is achieved by simultaneous illumination with ir light during pumping (Fig. 5).

From the spectral distribution of the shortcircuit current, it is known⁶ that even photons with energies less than the bandgap can create electron-hole pairs in GaP. If a plot of Q against the photon energy of the pump light used to empty the acceptor levels is compared with the spectral sensitivity of the shortcircuit current (Fig. 6), the same low-energy sensitivity edge is found at about 1.5 eV . Although this value nearly corresponds to the distance of the acceptor level from the conduction band edge, the value is somewhat too low to exclude the possibility that also other levels are involved in the excitation of free electron-hole pairs with extrinsic light.

Because of the large binding energy of the acceptor levels responsible for the hole capture, long storage times are observed in our diodes. The stored charge Q decreases typically 30% after 1 h in darkness at room temperature (Fig. 7). From measurements of Q as a function of the waiting time t_w the order of magnitude of the thermal release factor γ of the acceptor levels

involved in the hole capturing can be estimated. If the assumption is made that only one level is present and that

$$da^0(t)/dt = -\gamma a^0(t),$$

where $a^0(t)$ is the concentration of the empty acceptor levels at the time $t = t_w$, a plot of $\log Q$ as a function of the waiting time t_w should give a straight line. Experimentally, this is more or less confirmed at larger waiting times giving a value of about $5 \times 10^{-6} \text{ sec}^{-1}$ for γ .

The results described hitherto are also obtained when instead of light a forward bias is used for excitation. This is illustrated in Fig. 1 where Q is plotted as a function of the current flowing through the diode a time $t_p = 10^4 \text{ sec}$ in order to avoid incomplete excitation. These results indicate that Q saturates for currents in excess of $5 \times 10^{-6} \text{ A}$. This current value corresponds to a forward bias of about 1.3 V as it is seen from the I-V curve. Apart from the arguments presented later, it

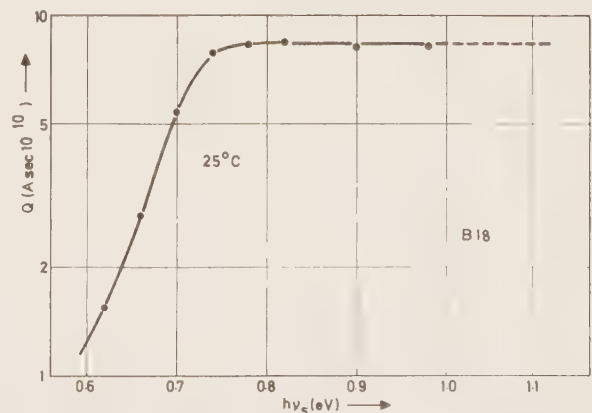


FIG. 3. Stored charge Q as a function of the ir photon energy $h\nu_s$. $t_p = 15 \text{ sec}$, $t_w = 30 \text{ sec}$, $t_s = 100 \text{ sec}$ (see text).

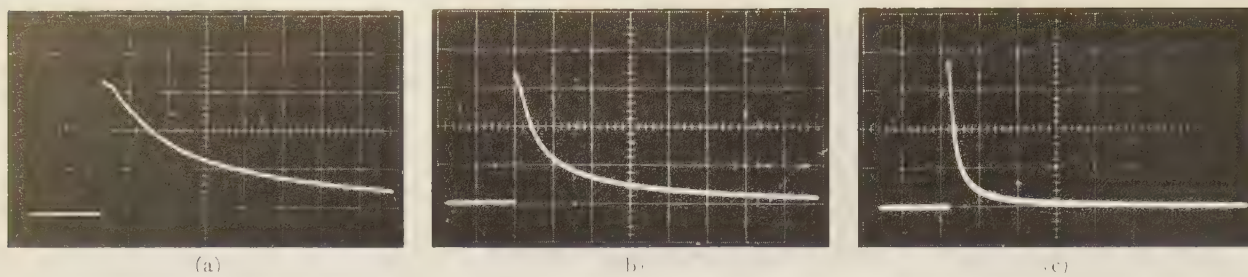
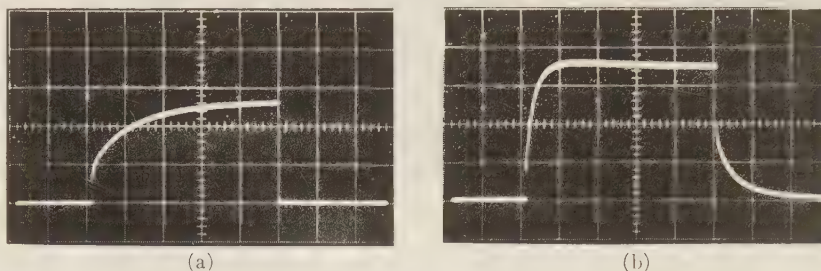


FIG. 4. Time dependence of the shortcircuit current ($Q2$) for three different ir photon energies $h\nu_s$: (a) $h\nu_s = 0.8$ eV, vertical scale 0.3 nA/div; (b) $h\nu_s = 0.88$ eV, vertical scale 1.1 nA/div; (c) $h\nu_s = 1.0$ eV, vertical scale 5 nA/div. Horizontal scales 0.5 sec/div.

FIG. 5. Time dependence of the shortcircuit current i_{sc} ($Q2$) caused by extrinsic light (0.79μ) (a) without and (b) with simultaneous ir (1.2μ) illumination. Vertical scale 1 nA/div, horizontal scale 1 sec/div.



might be expected that hole capture is more effective with minority carrier injection than with extrinsic light because in the latter case, a certain refilling of the acceptor levels with electrons from the valence band cannot be avoided, for if no refilling took place, there could not be any extrinsic steady state shortcircuit current. A comparison between Figs. 1 and 3 shows

indeed that the Q values obtained with current excitation are larger than those with extrinsic light. Furthermore, when the diode after being biased in the forward direction with $V > 1.3$ V is illuminated with photon energies $1.5 \text{ eV} < h\nu < 2 \text{ eV}$, this refilling causes a transient shortcircuit current that is superimposed on the total current (Fig. 8).

It has already been pointed out that the creation of a shortcircuit current demands both free holes and free electrons.¹³ By illuminating the diode with ir light after pumping, not only free holes but also free electrons have to be excited. In the neutral n region this can in principle be achieved by simultaneous excitation of electrons from donor levels. In our case, however, where the Fermi level in the n region is situated relatively close to the conduction band, the electrons stored

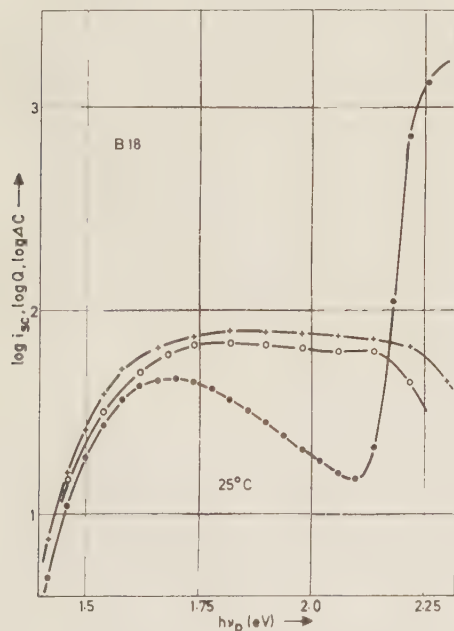


FIG. 6. Logarithm of the capacitance change ΔC ($\circ-\circ$) and logarithm of the stored charge Q ($+--+$) both as a function of the extrinsic photon energy $h\nu_p$ used for pumping. $\bullet-\bullet$ denotes the spectral sensitivity of the logarithm of the shortcircuit current i_{sc} .

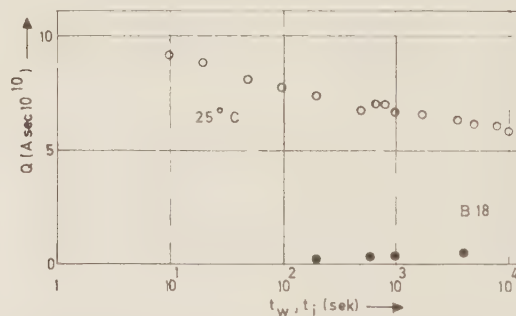


FIG. 7. Stored charge Q ($\circ$) as a function of the logarithm of the waiting time t_w ($t_p = 15$ sec). $\bullet$ denotes the charge Q obtained at room temperature a time t_i after ir illumination.

¹³ See, for instance, R. Wiesner, *Halbleiterprobleme III* (F. Vieweg & Sohn, Braunschweig, 1956), p. 59; T. S. Moss, *Semiconductors and Semimetals* (Academic Press Inc., New York, 1966), p. 205.

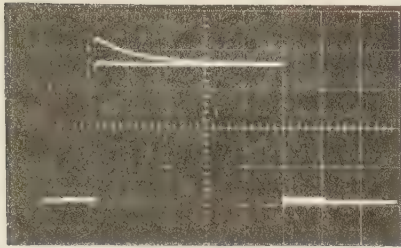


FIG. 8. Time dependence of the shortcircuit current ($Q2$) obtained with extrinsic light (0.65μ) without any bias (lower curve) and when the diode has been biased with 1.3 V previously (upper curve).

due to the charge exchange would be thermally released and no long storage times can be expected in contrast to the experimental results. If however, hole capturing takes place in the positive space-charge region, two effects can become apparent. Either charge exchange happens with no change in charge density, or the excited electrons will be trapped outside the positive space-charge region causing a change in the charge density in this region. The first case is rather unlikely because, among others, the low concentration of deep donor levels³ could not account for the large Q values observed. In the second case, a change in the diode capacitance should be found after illumination, because the charge density of the space-charge region is directly correlated to the transition-layer capacitance of the diode. This is in agreement with experimental results. A clear change in the transition layer capacitance is observed before and after illumination of the diode with photon energies larger than about 1.5 eV, showing at the same time that charge exchange in the positive space charge region obviously does not play a dominant role. According to this explanation, $\Delta C = C_a - C_0$ should be correlated with Q , where C_0 is the diode capacitance before pumping and C_a the capacitance in darkness after the source of excitation has been removed. Plotting ΔC against the photon energy of the (pump) light used for excitation, it is clearly seen (Fig. 6) that this indeed is the case and that the same low-energy sensitivity edge as for the shortcircuit current is obtained. Furthermore, if ΔC is plotted as a function of the ir photon energy after the diode has been excited with photon energies $h\nu > 1.5$ eV, a decrease in ΔC is found for photon energies where Q increases (Fig. 9). It is also observed that ΔC is not affected by photon energies less than 0.55 eV and that ΔC is rather small already for photon energies of 0.8 eV, thus indicating that the junction capacitance is nearly returned to the value of thermal equilibrium. This shows that ΔC , Q , and i_{sc} are generated by the same excitation processes giving rise to hole capturing that cause a change in the transition-layer capacitance after the source of excitation has been removed, and that can be returned to thermal equilibrium by illuminating the diode with ir light, whereby a transient shortcircuit current is caused.

Assuming an abrupt p - n junction, these experimental results can be readily explained using a simple model that takes into account the presence of acceptor levels in the transition region in the bulk of the junction, as due to the compensation of the starting material with copper. The energy band diagram of the p^+-n junction used in the present analysis is illustrated in Fig. 10(a). From previous investigations of the bulk material, it is known^{3,5,8} that besides deep-lying acceptor levels, further impurity levels with large binding energy have to be taken into account, although their concentration is rather low. These levels have been assumed to be donor levels. Restricting ourselves to one acceptor level E_a and one donor level E_k , the transition region of the junction can be divided in three regions by the boundaries x_a and x_k according to different charge densities. x_a and x_k are determined from the interception of the Fermi level and the acceptor and donor levels, respectively. In thermal equilibrium, the charge densities in the three regions are $\rho(0 < x < x_a) = e(N_d + N_k)$, $\rho(x_a < x < x_k) = e(N_d + N_k - N_a)$ and $\rho(x_k < x < W) = e(N_d - N_a)$, where N_d is the concentration of the ionized shallow donor levels, responsible for n -type conductivity in the starting material and N_k and N_a the electrically active concentration of the deep donor levels and acceptor levels, respectively [Fig. 10(b)]. Assuming that after illumination with photon energies $h\nu > 1.5$ eV, all acceptor levels in the space-charge region are empty, only two regions are left with net charges $\rho(0 < x < x_k') = e(N_d + N_k)$ and $\rho(x_k' < x < W) = eN_d$, thus causing a decrease in the width of the space-charge region [Fig. 10(c)]. Because of the large binding energies of both the donor and acceptor levels, the capacitance of the junction in thermal equilibrium at sufficiently high frequencies is given by¹⁴

$$C_0 = F \cdot \epsilon / W, \quad (1)$$

where F is the area of the junction. Using $C_a = F \cdot \epsilon / W'$

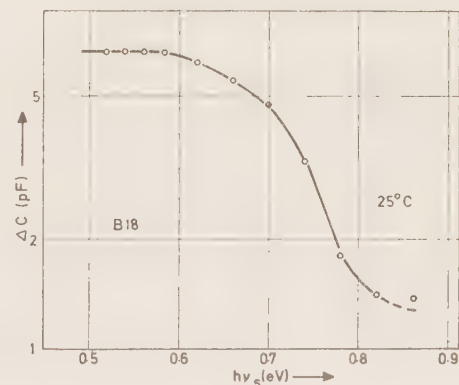
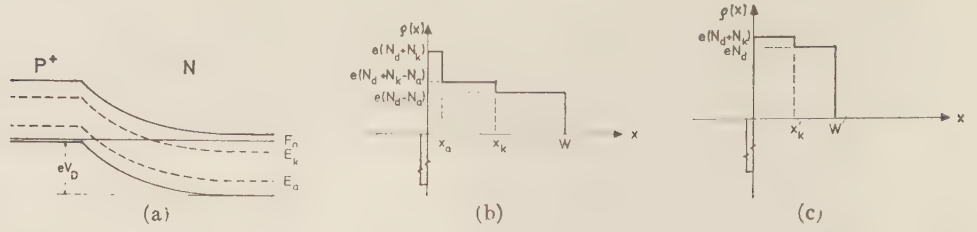


FIG. 9. Capacitance change ΔC as a function of the ir photon energy $h\nu_s$ (see text).

¹⁴ C. T. Sah and V. G. U. Reddi, IEEE Trans. Electron Devices ED-11, 345 (1964).

FIG. 10. (a) Energy-band model; (b) charge distribution in thermal equilibrium; (c) charge distribution after pumping.



it follows that $\Delta C = C_a - C_0 = F \cdot \epsilon [(1/W') - (1/W)] > 0$ because of $W > W'$, which agrees with the experimental results. Refilling all the empty acceptor levels by illuminating the diode with ir photon energies $E_a < h\nu < E_g - E_k$ a transient shortcircuit current is created representing a charge

$$Q = F \cdot e \cdot N_a \cdot W', \quad (2)$$

whereby the junction capacitance is changed. Both ΔC and Q can be calculated and compared with experimental results if W and W' are known. A relation

$$W - x_a = [1/(N_d - N_a + N_k)] [2\epsilon\phi_k/e(N_d - N_a)]^{1/2} \{N_k + [(N_d - N_a)^2(\phi_a/\phi_k) + N_k(1 - N_a)(\phi_a/\phi_k) - N_k(N_d - N_a)]^{1/2}\} = \beta \cdot \gamma, \quad (5)$$

$$\phi_a = (E_{F_n} - E_a)/e,$$

$$\phi_k = (E_{F_n} - E_k)/e.$$

From Eqs. (3), (4), and (5), the wanted voltage dependence of the junction width W can be calculated, giving

$$W = [\beta/(N_d + N_k)] (N_a\gamma + N_k + \{(N_a\gamma + N_k)^2 + (N_d + N_k)[(2\epsilon/e\beta^2)(V_D - V) - N_a\gamma^2 - N_k]\}^{1/2}). \quad (6)$$

By inserting Eq. (6) in Eq. (1), the voltage dependence of the junction capacitance is obtained:

$$C_0 = \frac{F \cdot \epsilon \cdot (N_d + N_k)}{\beta [N_a\gamma + N_k + \{(N_a\gamma + N_k)^2 + (N_d + N_k)[(N_d - N_a)/\phi_k](V_D - V) - N_a\gamma^2 - N_k\}^{1/2}]}. \quad (7)$$

For $N_d \gg N_k$, this can be transformed to:

$$C_0 = C_0' \cdot \{[\phi_k(N_a\gamma + N_k)^2/N_d(N_d - N_a)(V_D - V)]^{1/2} + [1 + \phi_k(N_a\gamma + N_k)^2/N_d(N_d - N_a)(V_D - V) - (N_a\gamma^2 + N_k)\phi_k/(N_d - N_a)(V_D - V)]^{1/2}\}^{-1}, \quad (8)$$

where

$$C_0' = F[eeN_d/2(V_D - V)]^{1/2},$$

and is the capacitance of the junction without deep levels. Similar to the one-level case calculated by Sah and Reddi,¹⁴ C_0 decreases with increasing concentration of acceptor levels because of the increase in W . Consequently when the diode is illuminated with photon energies $h\nu > 1.5$ eV and the electrically active concentration of acceptor levels is reduced, the junction capacitance will increase. This increase in capacitance is also observed when the source of excitation is removed, because the captured holes will stay in the acceptor levels due to the large binding energy, in agreement with the experiment. It is also clear from Eq. (7) that this rise in capacitance should increase with the degree of compensation. Although the compensation was probably rather low in our diodes and

between the applied voltage V and the width W of the junction is however, readily obtained from the solution of the Poisson equation using the simple charge distribution shown in Fig. 10(b) and equalizing the junction width W with the positive space charge region. The solution is

$$V_D - V = (e/2\epsilon) [N_a x_a^2 + N_k x_k^2 + (N_d - N_a) W^2], \quad (3)$$

where

$$W - x_k = [2\epsilon\phi_k/e(N_d - N_a)]^{1/2} = \beta, \quad (4)$$

therefore the change in capacitance after illumination quite small (at most 15%), it is nevertheless evident from Eq. (7) that a large increase can be expected with properly doped junctions.

The results given in Eq. (7) can be readily proved experimentally by measuring the junctions capacitance as a function of the applied voltage in darkness (Fig. 11). In contrast to junction without deep levels,¹⁵ and in agreement with Eq. (7), no linear relationship has been found between C_0^{-2} and V , in all those diodes, in which storage effects have been observed. In the case of diode B 18, the best fit between Eq. (7) and the experimental results has been obtained when $N_d = 6 \times 10^{16} \text{ cm}^{-3}$, $N_a = 4 \times 10^{16} \text{ cm}^{-3}$ and $N_k = 10^{16} \text{ cm}^{-3}$, assuming $\phi_k = 0.5$ V (solid line in Fig. 11). These values clearly correspond to the series resistance of the diode

¹⁵ W. Shockley, Bell System Tech. J. 28, 436 (1949).

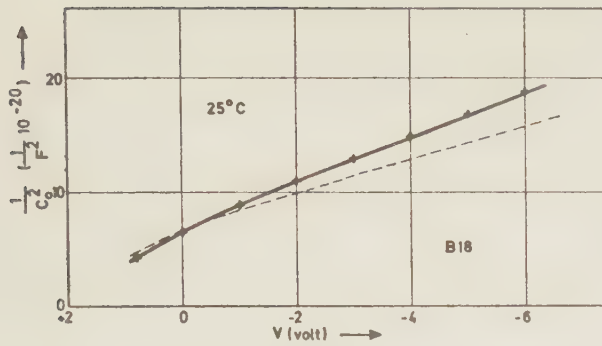


FIG. 11. Plot of C_0^{-2} against bias. + denotes experimental and — calculated values using Eq. (7) in the text. The dotted line corresponds the best fit of Eq. (10b) in Ref. 14 for the one-level case.

and agree with previous investigations which indicated that the concentration of the deep donor levels is only small. Furthermore, the N_a/N_d value for the degree of compensation is not in contradiction to the observed ΔC values.

The N_a value obtained from this experiment can be employed for an estimation of Q . If it is assumed that all acceptor levels are emptied during excitation and that at the same time all deep lying donor levels are filled, Eq. (9) can be used to calculate W' in order to estimate the lower limit of Q . Taking $F=1.5 \times 10^{-3} \text{ cm}^2$ and inserting $N_a=4 \times 10^{16} \text{ cm}^{-3}$ in Eq. (2), this gives $Q_{\text{cal}}=2 \times 10^{-10} \text{ A} \cdot \text{sec}$ which is lower than the experimental results, as expected. Somewhat higher calculated Q -values are obtained when no assumption is made on the filling up of the deep lying donor levels.

Using Eq. (2), we tacitly assumed that all acceptor levels in the region $0 < x < W'$ are filled by electrons with ir illumination. This means, however, that thermal equilibrium is not obtained immediately after ir illumination, because in thermal equilibrium acceptor levels in the region $0 < x < x_a$ are empty. It should there-

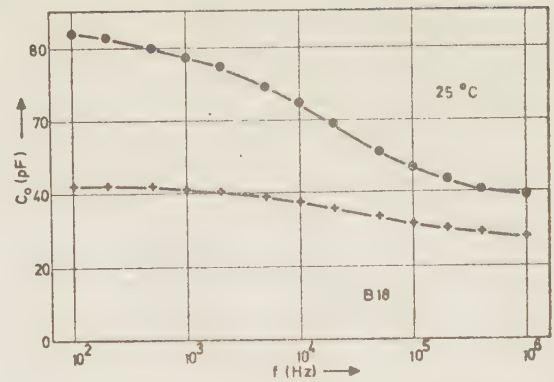


FIG. 12. Transition-layer capacitance C_0 of diode B 18 as a function of frequency with -2.5 V (+—+) and without (●—●) reverse bias.

fore be expected that the junction capacitance is somewhat smaller directly after ir illumination than in thermal equilibrium. This is in agreement with experimental results. The capacitance of diodes showing storage effects increases in darkness after the source of ir illumination is removed, until thermal equilibrium is reached. On the other side the capacitance in thermal equilibrium decreases after ir illumination.

That thermal equilibrium is not reached after ir illumination is also confirmed by transient photoeffects without pumping. With repeated ir illumination the diodes do not show any photoeffect as long as the time t_i between ir illuminations is short. This ceases to be the case for sufficiently large t_i values. Figure 7 illustrates the increase in charge represented by a transient short-circuit current obtained by thermal pumping at room temperature as a function of t_i .

In conclusion we only want to add that the low frequency capacitance C_{d0} for a junction with two deep levels has been calculated using the method of Sah and Reddi¹⁴ giving

$$C_{d0} = \frac{F \cdot \epsilon \cdot (N_d + N_k)}{\beta \{ (N_a \gamma + N_k)^2 + (N_d + N_k) [(N_d - N_a) / \phi_k] (V_D - V) - N_a \gamma^2 - N_k \}^{1/2}} \quad (10)$$

As in the one-level case, C_{d0} is always larger than C_0 for all applied voltages. This is illustrated in Fig. 12 where the junction capacitance is plotted as a function of frequency. A closer inspection of Eqs. (7) and (10) reveals that the difference between C_0 and C_{d0} decreases with increasing reverse bias. Because both values decrease with reverse bias this means that C_{d0} decreases faster than C_0 as illustrated in Fig. 12. Calculating

$$[C_0 / (C_{d0} - C_0)]^2 = [(N_d + N_k) (N_d - N_a) / (N_a \gamma + N_k)^2 \phi_k] (V_D - V) - [(N_a \gamma^2 + N_d) (N_d + N_k) / (N_a \gamma + N_k)^2] + 1, \quad (11)$$

it is seen that the above ratio should be linearly dependent on the applied voltage. This has been found independent, whether saturation has been obtained at low frequencies or not. In agreement with Auth¹⁶ it is

therefore not convincing that such a linear dependence is really a sensitive check.¹⁴

IV. CONCLUSIONS

Previous investigations indicated that acceptor levels with large binding energy and hole-capture coefficient

¹⁶ J. Auth, Phys. Status Solidi 27, 653 (1968).

exist in copper-doped GaP. In this paper, it has been shown that these acceptor levels can be used for charge storage in the transition region of alloyed diodes made of GaP-Cu. Charge storage is achieved by hole capture in the acceptor levels. Holes are created either by illumination or electrical injection of the forward biased junction. The charge stored in the acceptor levels amounts typically to 10^{-9} A·sec, at junction areas of $c:a$ 10^{-8} cm² and can be released by ir illumination causing a transient shortcircuit current without any externally applied voltage. In contrast to photoconductors, these storage effects are easily detected in diodes because normally a shortcircuit current is not generated with photon energies less than half the band-gap. The lowest ir photon energy exhibiting a transient photoeffect corresponds to the binding energy of the acceptor level. At room temperature, the stored charge is therefore only little affected by thermal ionization processes during the first hour. Due to the

hole capturing also the charge density in the transition layer and therefore the diode capacitance is changed. This change in capacity has the same time constant as the stored charge Q and can be quenched by the same ir photon energies that cause the transient photoeffect. The experimental voltage dependence of the transition layer capacitance of selected diodes is in agreement with theoretical considerations taking into account both acceptor levels and donor levels with large binding energies.

ACKNOWLEDGMENTS

The authors wish to thank G. Björklund and M. O. Ottosson for valuable discussions. They are also grateful to Philips Zentrallaboratorium GmbH, Aachen for supplying the Cu-doped GaP material used in this investigation and to the Swedish Council for Technical Research for financial support.

OS/HL.

SEMICONDUCTOR ELEMENT
WITH CHARGE STORAGE EFFECT.

Abstract of the disclosure.

A semiconductor element with a charge storage effect comprising a semiconductor material with a barrier including a space charge region. The space charge or depletion region may be provided by e.g. a PN-junction, a metal-semiconductor junction or a metal-insulator-semiconductor junction. The semiconductor material per se has at least one deep-lying impurity level, which can be either a donor or acceptor level, from which charge can be transferred to the valence or conduction band. In another embodiment, a semiconductor material may have two impurity levels between which charge can be transferred.

Related application.

This application is a continuation-in-part of our copending application Serial No. 314,073, which in turn is a continuation of our Serial No. 42,118, filed on June 1, 1970.

The Present Invention

The present invention comprises a semiconductor element with charge storage, that is, a semiconductor wherein electric charges can be moved between different energy levels and/or energy bands.

It is well known that charge restorage processes can be obtained in semiconductor material. These processes involve charge being transferred between different levels in the semiconductor material by means of light. In transfer between two such levels, one level must be at least partly empty so that carriers from the other level, which must be at least partly occupied, can be transferred. The two levels must then initially be substantially on either side of the Fermi level. The light which performs a transfer from the initial charge state to a new charge state is called the pumping light. It must have a photo-energy such that it can release carriers from the occupied level so that the carriers can be transferred to either the valence band, the conduction band or a second impurity level. A remaining charge storage can be obtained if the binding energy of the impurity level or levels is so large that the thermal ionization is very small and interaction between the level is negligible. In order to return the carriers to the initial level, the semiconductor material must be illuminated with a reset light. The reset light must have sufficient photoenergy so that the previously emptied level is at least partially refilled. The condition that when two impurity levels are used, the impurity levels involved in the process should initially be located on either side of the Fermi level requires a highly compensated material which is often rather difficult to produce.

Charge restorage processes of the type mentioned above have been described in the literature, particularly an article by H.G. Grimmeiss and G. Olofsson: "Storage Effects and Photoconducting GaP-Cu", Phys. Stat. Sol. Vol. 28 (1968) page 547-554.

When a homogeneous semiconductor material with two impurity levels, on either side of the Fermi level, is excited by means of pumping light, pairs of electron-holes are produced. The movable holes are captured by the occupied locations in the acceptor level and the movable electrons are captured by the unoccupied locations in the donor level. By this mechanism a charge transfer takes place.

It is an object of the present invention to obtain a semiconductor element wherein remaining charge storage can be achieved without requiring the material to present characteristics which are technically difficult to obtain. The particular requirements, stated above, to achieve the impurity levels lying on either side of the Fermi level are obviated by the use of the present invention. This is effected by providing the semiconductor element with a barrier having a space charge region. A barrier is a junction between two solids across which the movement of electric charges is not symmetrical. Such a barrier can be obtained by a PN-junction, a metal-semiconductor-junction or a metal-insulator-semiconductor-junction. In case of a metal-insulator-semiconductor-junction no charges will pass across the junction.

The presence of a barrier with a space charge region in the material results in the Fermi level lying between the levels involved in the restorage process at some position in the material since the Fermi level at the junction goes from the vicinity of the conduction band on the N side to the vicinity of the valence band on the P side.

A semiconductor element, wherein charge storage can be caused by illumination with light, can be utilized for a plurality of applications such as light detection, light integration, optical memory storage and capacitance variation.

In a diode it is possible, in principle, to have charge restorage processes in three regions. These regions are the neutral part of the P-side, the depletion region, and the neutral part of the N-side. It should be noted that in the depletion region of the PN-junction it is possible to obtain storage in two different ways. One of the storage processes occurs in the manner described above, whereby no change of the

space charge density is required. In the other process one carrier type replenishes the impurity level, while the other is moved by the field which causes a change of the space charge density. and thus, a change of capacity over the depletion region. In restorage in the neutral region it is only possible to have a storage of carriers according to the first mentioned process.

Brief Description of the Drawings.

Figures 1A-1D schematically illustrate an energy band model for a homogeneous semiconductor material in various states:

Figures 2A-2B schematically illustrate an energy band model for a semiconductor material with two impurity-levels and a PN-junction in various states; and

Figures 3A-3D schematically illustrate an energy band model for a semiconductor material with one impurity level and a metal-semiconductor-junction in various states.

Background of the Invention

Figures 1A-1D illustrate a homogeneous semiconductor material with two impurity levels, each lying on different sides of the Fermi level. One impurity level consists of an occupied acceptor level a and the other consists of an unoccupied donor level k . The condition that the Fermi level E_F should be located between these two levels has been indicated in the drawing. In a material with a wide band gap such as GaP (2.25 eV), it is rather simple to obtain impurity levels with large binding energies, i.e., which are deeply lying. This means that the probability of thermal ionization at room temperature is very small. In those cases and with those materials wherein the impurity levels have less binding energy, charge transfer can also be achieved with a requirement that for lasting charge storage the operating temperature would have to be reduced. The acceptor level a is obtained by means of Cu-doping of GaP, which has the feature that its capture cross section for electrons in the conduction band is small and less than the corresponding value for the donor level k , while its capture cross section for holes in the valence band is large. The donor level k is obtained

by means of O-doping. When excited by means of pumping light, pairs of electron-holes are produced. As indicated in Figure 1B, the movable holes formed, indicated by +, are captured by the occupied locations in the acceptor level a and the movable electrons formed, which are indicated by -, are captured by the unoccupied locations in the donor level k. The result, illustrated in Figure 1C, shows the material after illumination with pumping light. A charge transfer has taken place between the levels a and k. This situation will remain for a certain period of time, the duration of which depends mainly upon the temperature, since the probability of a direct transfer between the levels a and k is very small. The charge transfer enables the excitation of electrons from the valence band to the level a, or from the donor level k to the conduction band, by renewed illumination, termed a reset light, as indicated in Figure 1D. The minimum photoenergy for such an excitation is defined by the energy spacing between the level a and the valence band or the energy spacing between the donor level k and the conduction band. On such an excitation, free carriers are produced, which can take part in the conduction mechanism. As the level a is occupied, this possibility of forming free carriers is reduced. Thus, in case the material is utilized as a photoresistor, a transient change of the resistance is obtained.

Description of the Invention

Figure 2A illustrates, as an initial state, a PN-junction in equilibrium with two impurity levels, similar to the previous description. It should be noted that in semiconductor materials with junctions it is not necessary to have two impurity levels, and this embodiment will be explained with respect to Figure 3. However, Figure 2A shows a region L wherein the previous discussion can be applied since the Fermi level lies between the two impurity levels. At least two different situations can be observed. The electrons formed by the pumping light excitation (which

are indicated in Figure 2B) can be captured directly by the level k (which is indicated by the arrow A), which corresponds to a charge transfer without change of the space charge density, or these electrons may be moved within the depletion region by means of an electric field or a concentration gradient (which is indicated by the arrows B and B'). In the latter cases, an increase in the positive space charge density occurs on the N-side and this fact causes a reduction of the width W_n of the N-depletion region. The junction capacitance, which is inversely proportional to the width $W_n + W_p$, is then increased. The capacitance change obtained will remain in accordance with the process described in connection with the charge restorage. On illumination with reset light, which can excite electrons from the valence band to the level a , free holes are obtained, which together with the previously stored electrons can form a photocurrent. By this process the value of the capacitance can be returned to its initial value.

In both the depletion region and the neutral regions a storage process can thus be obtained by means of restorage processes, but in addition in the first mentioned region the space charge density can be affected and thereby the width of the depletion region can be changed. This will result in varying the junction capacitance. Changes of capacitance caused by illumination with pumping light can then be cancelled by illumination with reset light with proper photoenergy, which reduces the degree of occupation of the impurity levels filled by the pumping light energy. With a particularly defined geometry and doping concentration it is possible to obtain a predetermined capacitance change, which is also related to the wave length of the pumping light or the illumination time. A simultaneous illumination with pumping light and reset light affords additional possibilities of continuous tuning of the amount of the capacitance such as by changing the relation between the intensities of the two illuminations.

The storage described above can also be observed based on the photoeffect of the PN-junctions. The amount of storage is defined by the rate of replenishment of the impurity centres, said rate in turn being defined by the

intensity of the pumping light. In a corresponding manner the efficiency of the resetting process is dependent on the intensity and energy of the reset light. This means that it is possible to have a low pumping light intensity during a long time and then measure the charge stored thereby during a short time by selecting the photoenergy and intensity of the reset light so that the retransfer process becomes highly efficient. The photoenergy of the reset light can be selected so that it cannot in general produce any photoeffect by itself. On simultaneous illumination with the pumping light a sensitivity for lower energies is obtained by means of the processes indicated, the lower energy edge of which is defined by the impurity levels involved in the reset process. This can be performed by modulating the reset light under simultaneous constant illumination with pumping light and thereafter amplifying the changes caused by means of the modulated light. Pumping during a long time, however, will give remaining effects only if the impurity levels involved in the process have large binding energies such as copper and oxygen in GaP. The expression "large binding energies" is equivalent to "deep lying impurities" and indicates that the binding energy for the level is much greater than kT , where k is Boltzmann's constant and T is the absolute temperature. In GaP-diodes which are doped with copper as an example, a charge storage of 10^{-5} . As/cm² has been measured, which declined by about 30% in one hour at room temperature. The related capacitance change was 15% and had a corresponding time factor. Since GaP has a forbidden gap width of 2.25 eV, at room temperature, and the Cu level is spaced from the valence band by about 0.7 eV, it is spaced from the conduction band by about 1.55 eV. As a result the pumping light must have a wave length of 8000 angstroms or less and the reset light must have a wave length greater than 8000 angstroms, but less than 17.800 angstroms. The resistivity of GaP doped with Cu may be between 1-10 ohm/cm corresponding to a free carrier concentration of about 10^{16} - 10^{18} atoms/cm³. The PN-junction can be obtained by alloying an Au/Zn bead to the GaP crystal. In the diode the activated pumping light can be replaced by a voltage in

the forward or reverse direction. We have produced the remaining charge storage effect in elements of GaP, GaAs, Si, and ZnSe with deep level impurities of O and Cu in GaP; O and Co in GaAs; Au in Si, and Mn in ZnSe. The depletion region in these elements has been produced by an alloyed PN-junction, an epitaxially grown PN-junction, a metal-semiconductor-junction and a metal-insulator-semiconductor-junction.

Figures 3A-3D schematically illustrate an energy band model for a semiconductor material including a metal-semiconductor-junction with one impurity acceptor level. Figure 3A shows the material in thermal equilibrium. Figure 3B shows the formation of electron-hole pairs by reason of pumping light. The holes are captured in the impurity level "a" causing a change in the net concentration in the depletion region. Figure 3C shows the result of the pumping light caused charge transfer. This new quasi-equilibrium state has a smaller width of the depletion region giving a higher and quasi-constant depletion layer capacitance. In Figure 3D reset light of energy just enough to refill the level a illuminates the component. This light returns the component to its thermal equilibrium state shown in Figure 3A. The width of the depletion region has again changed back to its equilibrium state. The released charges caused by the reset light produces a photocurrent pulse which can be measured.

Satisfactory results have been achieved with an element having a body of N-type GaP which at least in the proximity of a formed barrier is doped with Cu in order to produce a desired acceptor level with large binding energy. The rectifying contact, i.e. the metal-semiconductor-junction, was made by evaporation of Au on the surface of the GaP body. One of the leads was connected to this Au-layer and the other lead is connected to an ohmic contact attached to the GaP body by alloying an Au/Zn bead. Close to the surface and under the evaporated Au layer we now have a depletion region which can be used in a similar way as the earlier described PN-junction.

Although Figures 3A-3D illustrate the charge mechanism in a device with an impurity acceptor level, the transfer mechanism itself is similar in instances in which the semiconductor contains an impurity donor level. Furthermore, the single impurity level of Figure 3 could be used in the PN-junction

device described with respect to Figure 2. The reason for this is that one impurity level can coact with either the valence or conduction band, both of which are always available. However, the use of two impurity levels, one acceptor level and one donor level, may increase the charge storage effect of the semiconductor element.

The charge mechanism in a metal-insulator-semiconductor-junction is principally the same as in a metal-semiconductor-junction according to Figure 3 and, therefore, has not been shown in the Figures.

To sum up, it is previously known that remaining charge storage effects can be obtained in semiconductor materials, e.g. GaP doped with Cu (copper) to provide a deep-lying acceptor level in the forbidden gap, when illuminated. This charge storage effect may be increased by doping the semiconductor material with e.g. O(oxygen) to provide also a deep-lying donor level in the forbidden gap. With two impurity levels, viz. one acceptor level and one donor level, the condition that the impurity levels should be located on either side of the Fermi level can easily be obtained by providing the semiconductor material with a barrier having a space charge region, said barrier being obtained by e.g. a PN-junction, a metal-semiconductor-junction or a metal-insulator semiconductor-junction. Furthermore, the use of one impurity level and a barrier will provide a semiconductor element having a capacitance over the barrier, said capacitance changing with the restorage of charges in the barrier and the capacitance changes remaining until the charges are returned to their original states, e.g. by means of reset light.

WHAT WE CLAIM IS:

1. A semiconductor element with charge storage effect comprising a body of semiconductor material of low resistivity having an impurity level in the forbidden gap, said impurity level being an acceptor level having a large binding energy at the operation temperature so that the probability of thermal interaction between said acceptor level and the conduction band or the valence band is very small, said level being able to optically interact with both the valence band and the conduction band, and the semiconductor body further presenting a barrier with a space charge region.

2. A semiconductor element according to claim 1, said barrier being a P-N junction.

3. A semiconductor element according to claim 1, said barrier being a metal-semiconductor-junction.

4. A semiconductor element according to claim 1, said barrier being a metal-insulator-semiconductor-junction.

5. A semiconductor element with charge storage effect comprising a body of semiconductor material of low resistivity having an impurity level in the forbidden gap, said level being a donor level having a large binding energy at the operation temperature so that the probability of thermal interaction between said donor level and the conduction band or the valence band is very small, said donor level being able to optically interact with both the valence band and the conduction band, and the semiconductor body further presenting a barrier with a space charge region.

6. A semiconductor element according to claim 5, said barrier being a P-N junction.

7. A semiconductor element according to claim 5, said barrier being a metal-semiconductor-junction.

8. A semiconductor element according to claim 5, said barrier being a metal-insulator-semiconductor-junction.

9. A semiconductor element with charge storage effect comprising a body of semiconductor material of low resistivity having a first impurity level in the forbidden gap, said first level being an acceptor level, and a second impurity level in the forbidden gap, said second level being a donor level, said impurity levels having large binding energies at the operation temperature so that the probability of thermal interaction between said impurity levels and between each impurity level and the band at the smallest distance from said level is very small, said impurity levels being able to optically interact with both the valence band and the conduction band, the semiconductor further presenting a barrier with a space charge region.

10. A semiconductor element according to claim 9, said barrier being a P-N junction.

11. A semiconductor element according to claim 9, said barrier being a metal-semiconductor-junction.

12. A semiconductor element according to claim 9, said barrier being a metal-insulator-semiconductor-junction.

FIG. 1A.

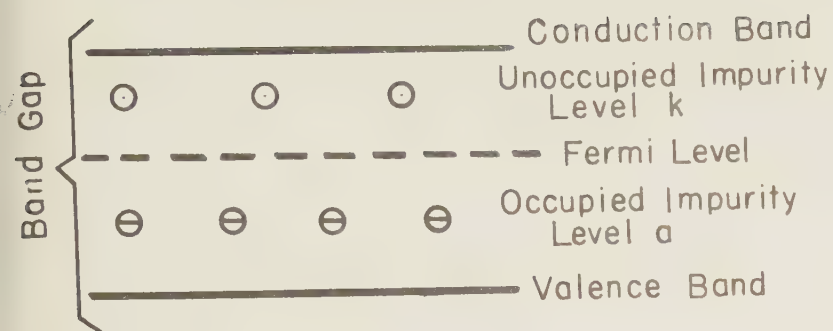


FIG. 1B.

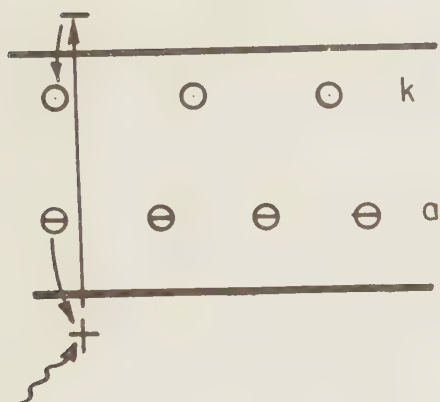


FIG. 1C.

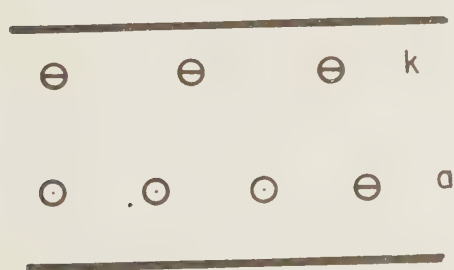


FIG. 1D.

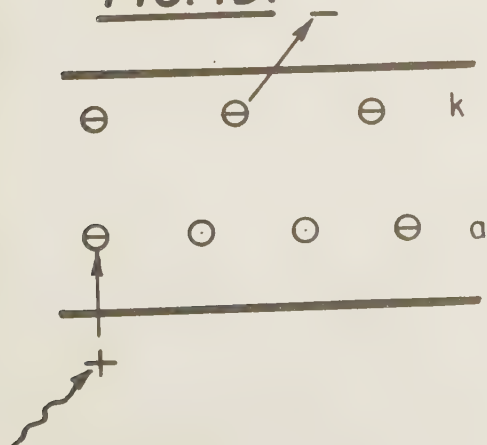


FIG. 2A.

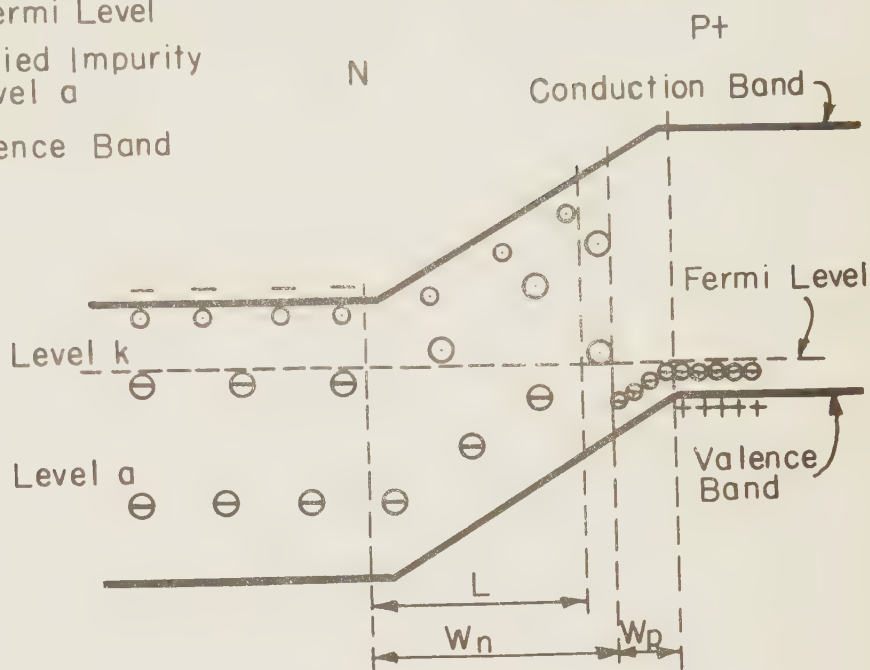


FIG. 2B.

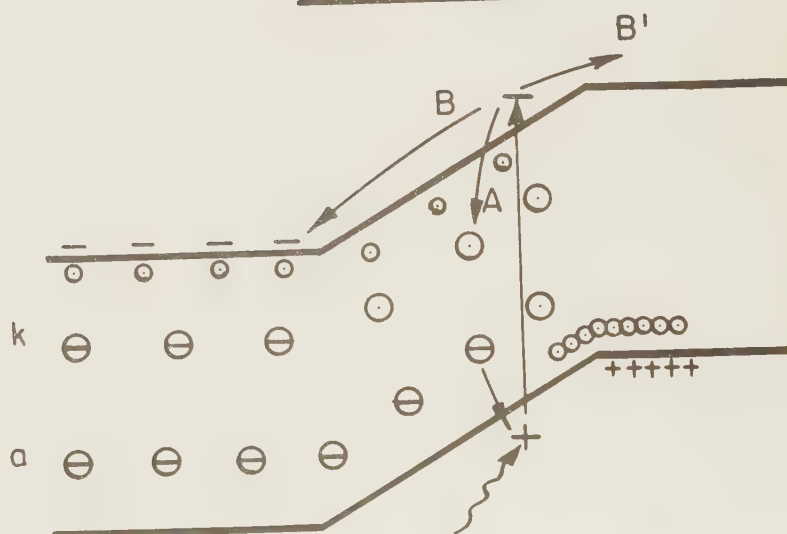


FIG 3 A

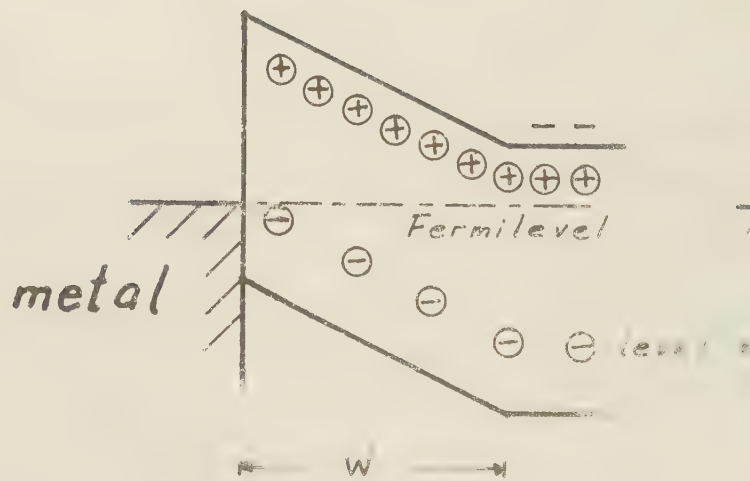


FIG 3 B

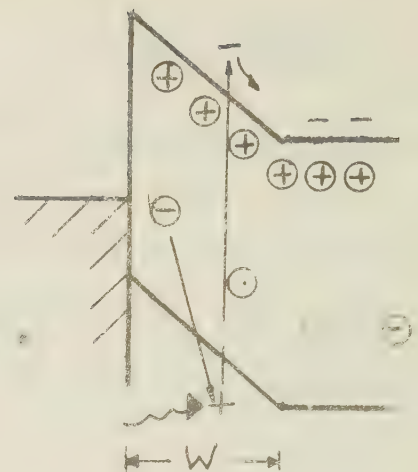


FIG 3 C

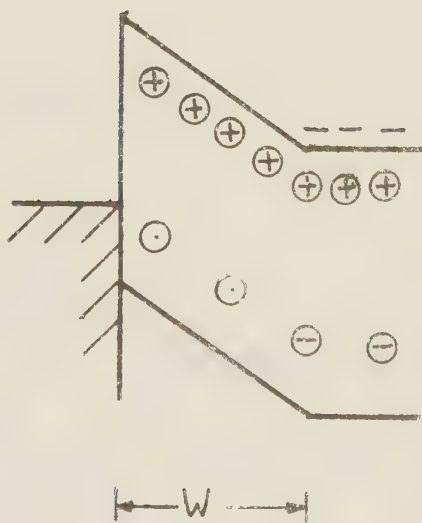
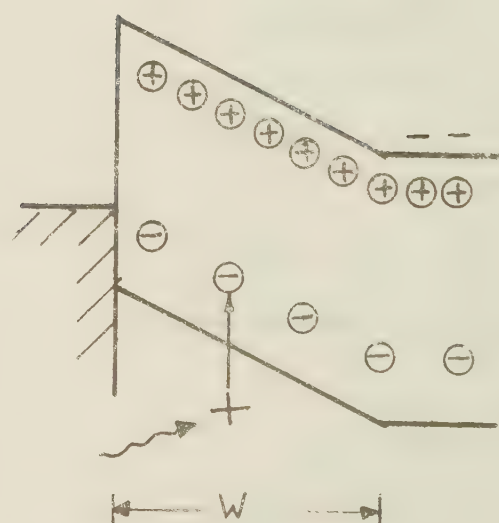


FIG 3 D



INVESTIGATION OF OPTICAL PROPERTIES OF A GaP MIS STRUCTURE *

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Abstract

It is shown how a MIS-structure in depletion stage can be used to study deep energy levels localized in the forbidden bandgap. Charge of excess minority carriers due to optical excitation is accumulated at the surface and is measured by the shift of the C-V-curve. The method is applied to GaP in which a deep-lying level at 0,7 eV from the valence band generally suggested to be a Cu-level is identified.

INTRODUCTION

Metal-insulator-semiconductor (MIS) structures have been extensively studied because of the increasing technological importance of planar silicon MOS-devices. MIS-structures are easy to make especially in silicon, and theoretical models (1) give a good background for the understanding of experimental results.

This has initiated the development of a method, presented in this paper, using MIS-structures to study some extrinsic properties, mainly deep impurity levels, of semiconductor materials. Such extrinsic properties are not only important for MIS-devices such as charge-coupled devices (2), where the method could be applied directly, but are more generally of increasing interest for the development of several other semiconductor components like light-emitting diodes etc. The process of making MIS-structures does not affect the bulk material very much, so a depletion layer, which is the main part of the structure used in the method and easily induced by an electric field, represents quite well the unprocessed material.

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The effect of a low recombination rate within the depletion layer in pn-junctions and metal barriers has earlier been used to study deep impurity levels (3, 4, 5, 6, 7). During the production of pn-junctions however, (by definition) the properties of the original material are changed. Furthermore it is difficult or impossible to get pn-junctions in some important materials like CdS or GaN. These drawbacks are avoided in MIS-structures. On the other hand the main disadvantage with metal barrier structures is the excitation of charge carriers from the metal.

The method described in this paper is based mainly on the measurement of the high frequency capacitance as a function of voltage (CV-curve). It is first theoretically shown how changes of this curve due to extrinsic illumination can be related to properties of deep impurity levels. To experimentally verify the theory, MIS-structures are made in GaP. Preparation and measurements fulfilling the given conditions are described. A new measurement principle using a feedback-controlled amplifier to control the width of the space charge region is the main contribution.

THEORETICAL BACKGROUND

A negative bias on the gate of a MIS-structure (fig 1) in an n-type semiconductor, will first deplete the semiconductor next to the insulator and then, depending on the concentration of the charge carriers and the surface potential, invert the semiconductor in a thin surface layer where minority carriers are accumulated. When such a surface layer is inverted, the width of the depletion layer will not further increase with increasing negative bias and the capacitance, measured at sufficiently high frequency not to allow the minority carriers to follow the test signal, will be constant. This is in contrast to a reverse biased pn-junction where accumulation of minority carriers is not observed and where all charge of the depletion region consists of the ionized impurity levels.

Using a simple model analogous to the one-sided abrupt pn-junction several important basic physical properties of a MIS-structure can be deduced (1). The high frequency capacitance as a function of a depleting bias (C-V-curve) can then be described by the following expression

$$\left(\frac{C_i}{C}\right)^2 = A(V-V_0) + 1 \quad \dots(1)$$

where

$$C_i = \frac{\epsilon_i \epsilon_0}{W_i} \quad \dots(2)$$

is the capacitance of the insulating layer per unit area

$$C = \left(\frac{1}{C_i} + \frac{1}{C_s}\right)^{-1} \quad \dots(3)$$

is the measured capacitance of the MIS-structure per unit area,

$$C_s = \frac{\epsilon_s \epsilon_0}{W_s} \quad \dots(4)$$

is the space charge capacitance per unit area and

$$A = \frac{2 C_i^2}{q (N_d - N_a) \epsilon_s \epsilon_0} \quad \dots(5)$$

N_d is the concentration of ionized donors of the semiconductor.

N_a is the concentration of ionized acceptors of the semiconductor.

ϵ_i is the permittivity of the insulator, ϵ_s is the permittivity of the semiconductor, ϵ_0 is the permittivity of free space,

$(8,859 \cdot 10^{-12} \text{ F/m})$, q is the magnitude of the electronic charge, W_i is the width of the insulating layer, W_s is the width of the space charge region, V is the applied bias on the gate,

$$V_o = \phi_{MS} - \frac{Q_{ss}}{C_i} \quad \dots(6)$$

Where ϕ_{MS} is the metal-semiconductor work function difference and Q_{ss} is the charge in the surface states.

Equation (1) is based on the assumptions that the dc bias varies slowly enough that the charge distribution in the semiconductor can be described by a quasi-equilibrium. The resistance outside the depletion region is neglected. In darkness the minority carriers can not be generated and/or transported at a sufficiently rapid rate to keep up with the high frequency test signal superimposed on the dc bias. This is also assumed for the change of the charges in the surface states even though their number is a function of the surface potential. The quantity $(N_d - N_a)$ is the uniform doping level within the semiconductor.

If a biased MIS-structure (fig 1) is illuminated with light of such an energy that electrons and holes are created, the capacitance will usually increase. Two reasons have been suggested in the case of inversion (8). One is that the faster generation of minority carriers creates inversion at a smaller bias and the other is that the excess electron-hole pairs cause a decrease of the surface potential which results in a reduction of the width of the space charge layer, with a corresponding increase of the capacitance, equation (4), (fig 2).

Regarding equations (1) and (6), which describe a MIS-structure in depletion, excess charge carriers, due to illumination with extrinsic light, could influence the surface charge Q_{ss} and the space charge density $N_d - N_a$. It is assumed that some of the acceptors, a , have an activation energy, E_a which is large related to the thermal excitation. Björklund and Grimmeiss (4)

have shown how the population of such a deep impurity level in a depleted region can be controlled to an almost set value with the help of a second light source. The following expression for the attaching photocurrent, J , has been deduced (4) when such a depletion layer in a pn-junction is simultaneously illuminated with extrinsic photons of different energy $h\nu_t$ and $h\nu_p$ respectively, (see fig 3):

$$J = K \cdot \frac{(\sigma_{cp} I_p + \sigma_{ct} I_t) (\sigma_{vp} I_p + \sigma_{vt} I_t)}{\sigma_{cp} I_p + \sigma_{ct} I_t + \sigma_{vp} I_p + \sigma_{vt} I_t} \quad \dots(7)$$

where K is a constant which Braun and Grimmeiss (5) later have expressed as

$$K = q (W_s - W_0) \cdot a \quad \dots(8)$$

for a -values small compared with the shallow background doping, N_d . W_0 is then the part of the space charge region in which extrinsic excitation is very small. The excitation processes in the neutral regions can normally be neglected because of recombination processes.

σ_{vp} , σ_{cp} , σ_{vt} and σ_{ct} (see fig 3) are the photoionization cross sections for the photon energies $h\nu_p$ and $h\nu_t$ respectively. The expression (7) is received for intensity ratios between I_t and I_p which experimentally are easily fulfilled (4). The recombination rate in the space charge region $W_s - W_0$ is neglected because of the high field strength. The excess minority carrier-concentration is small and thermal excitation processes can be neglected for sufficiently deep levels. If the photon energy $h\nu_t$ is chosen smaller than $E_g - E_a$ (i.e. σ_{ct} is equal to zero) and the intensity of the test light source, I_t , is much smaller than the population controlling light source, I_p , equation 7 can be used to get a reduced expression for the increase of the photocurrent ΔJ due to the additional illumination with photons of energy $h\nu_t$.

$$\Delta J = J(t+p) - J(p) = K \cdot I_t \cdot \sigma_{vt} \cdot \left(\frac{\sigma_{cp}}{\sigma_{cp} + \sigma_{vp}} \right)^2 \quad \dots(9)$$

For the increase ΔJ the rate-limiting process is the excitation of electrons from the valence band to the impurity level a.

The above theory for the depletion region of a pn-junction will now be applied to the depletion region in a MIS-structure. The excited minority charge carriers, which drift in the electric field of the depletion region towards the interface between the insulator and semiconductor, correspond to the photocurrent but accumulate as an excess surface charge, ΔQ_{ss} (fig 2). In depletion, however, this added surface charge neutralizes part of the gate charge and therefore less space charge is needed for the compensation, which is indicated in fig 2 by a smaller space charge width W_s . Equation 9 may thus be translated into a corresponding difference between surface charges. t is the time.

$$\Delta Q_{ss}(p+t) - \Delta Q_{ss}(p) = \Delta J \cdot t = \Delta Q'_{ss} \quad \dots(10)$$

Inserting equation (10) in equation (6) a voltage shift

$$\Delta V' = \frac{\Delta Q'_{ss}}{C_i} \quad \dots(11)$$

From equation (4) and (3) the width W_s can be calculated as

$$W_s = \frac{\epsilon_s \epsilon_o}{C_i} \left(\frac{C_i}{C} - 1 \right) \quad \dots(12)$$

Equation 8-12 now give

$$\begin{aligned} \Delta V' &= \Delta V(p+t) - \Delta V(p) = \\ \frac{t}{C_i} \cdot q \left[\epsilon_s \epsilon_o \left(\frac{C_i}{C} - 1 \right) - W_o \right] \cdot N_a \cdot I_t \cdot \sigma_{vt} \left(\frac{\sigma_{cp}}{\sigma_{cp} + \sigma_{vp}} \right)^2 &\quad \dots(13) \end{aligned}$$

This expression will later be used to study the optical ionization cross section σ_{vt} .

Material and experimental procedure

Sample preparation

In order to verify the above theory, MIS structures were made in wafers of Czochralski grown, single-crystal, n-type gallium phosphide which was not intentionally doped to get deep energy levels. The resistivity and charge carrier density were specified approximately to be 1,5 ohm · cm and $2 \cdot 10^{16} \text{ cm}^{-3}$ respectively. After mechanical polishing, the gallium phosphide wafers were cleaned according to an empirically well established program including ultrasonic cleaning in trihydroethylene and acetone, chemical etching in a solution of bromine in methanol, rinsing in ethanol and finally in deionized water.

The insulating layer consisted of silicon oxide which was deposited either by using silane oxidation or by RF sputtering. Aluminium squares were evaporated on the SiO_2 through a metal mask. The sides of the squares were 0,2 mm and the aluminium layer was about 1.500 Å thick. Some other metal layers such as thin transparent chromium-gold layers were tried.

Much work was done to get a good ohmic contact to the semiconductor substrate. It is very important not to get a high ohmic intrinsic region which the capacitance meter will interpret as a small capacitance and therefore make it impossible to measure the larger depletion layer capacitance which will be in series. The process which gave the best results consisted of alloying tin with the GaP in a gas (3 % HCl in H_2) at 550 C for 10-20 seconds.

Several samples were prepared following the above procedure. A very good reproduceability was achieved.



Experimental set-up and measurement

The high frequency (1 MHz) capacitance of the MIS-structure as a function of bias voltage, light intensity, light energy and time were measured. Great care was taken to avoid unwanted influences of the interface between the insulator and the semiconductor in the measurements and the interpretations. The parameters were changed at a rate slow enough to provide a necessary equilibrium. All measurements were performed at room temperature.

The sample, provided with two ohmic contacts to the semiconductor substrate in order to measure the contact resistance was placed with the SiO_2 side up on the stage of a micromanipulator which was placed on a microscope table, figure 1. A needle probe was used to contact the Al-squares and wires were soldered to the ohmic contacts. Light from a Zeiss double monochromator was focused by a mirror under the microscope table on the sample. By such an arrangement the light passed through the semiconductor crystal and an even illumination was reached. Another light source was a Reuter incandescent lamp with interference filter.

For the capacitance measurement two Boonton meters were used, both having 1 MHz testing signal and an amplitude less than 20 mV. Model 75 D for sensitive static measurement and model 71 A for dynamic measurement.

The output signal from the Boonton meters 71 A was either registered direct with a HP 7004 A X-Y-t recorder or put into a special amplifier, by which the bias was controlled in a way later described.

Experimental results

To check the prepared MIS-structures the C-V-curves were recorded, figure 4, curve a. Hysteresis due to moving ions in the insulator and other properties of the insulator such as leakage were carefully watched. According to equation (1) a plot of C^{-2} as a function of an applied voltage V should give a straight line. This can be seen in figure 5. From the slope of this straight line $N_d - N_a$ can be calculated (equations 1, 5). W_i is estimated to be 3200 Å by the colour of the silicon oxide layer. With $\epsilon_i = 3,8$ for silicon oxide the value of W_i can be checked by calculating C_i (equation 2). The calculated value, 4,1 pF, agrees quite well with the measured capacitance at positive bias (figure 4). With $\epsilon_s = 10$ for GaP $N_d - N_a$ can now be calculated and from equation (5) a value of $2,1 \cdot 10^{16} \text{ cm}^{-3}$ is found indicating that the preparation process has not changed the doping.

From figures 4, curve a, and 5 it can be seen that the capacitance is still increasing even at large applied voltages. Evidently the density of minority carriers, holes, is too low to facilitate inversion.

It has earlier been discussed how illumination may increase the number of minority carriers so that inversion is reached at a smaller bias voltage. A further increase of the bias will then not decrease the capacitance any longer. If the sample is illuminated with light of such an energy and intensity that the number of excess charge carriers is too low to invert the semiconductor surface, (at the used bias voltages), a change in gate charge must still be compensated by a change in space charge. Assuming no recombination in the space charge region the created excess minority carriers will accumulate at the surface and gradually take essential part in the compensation. This means that the width of the space charge, i.e. the measured capacitance, will not follow equation 1 but will be less dependant on the gate voltage as can be seen by curve b (figure 4) where the capacitance is recorded as a function of a slowly (0.05 Hz) increasing bias during illumination.

When the bias is decreasing, the accumulated charge will be more dominating and the capacitance will be even less dependant on the bias (curve c). The power of the hysteresis must of course be dependant on the amount of the accumulated charge. In curve d-e the energy of the light used is higher. The same effect will be the result if light of higher intensity is used. If the generated and accumulated minority carriers cause a surface charge high enough to compensate the gate charge, within the limits set by the amplitude of the scanning bias, the capacitance will stay constant as can be seen from curve f-g (figure 4).

In order to study the effect of illumination more in detail the measurements are preferably done in steady state. If the assumption that the recombination and/or thermal generation in the space charge region can be neglected is valid, the excess charge, ΔQ_{ss} , due to illumination, accumulated at the surface must remain at an almost constant value after the light is switched off. In figure 6 the capacitance is recorded as a function of time, t . At $t = t_{lon}$, light is projected on the MIS-structures and at $t = t_{loff}$ light is switched off. At $t = t_{Voff}$, the constant bias, V_1 , is off and at $t = t_{Von}$ on again. The curves are recorded at two different values of V_1 and for two different energies, $h\nu_p$ of the light. (A second light source, test light, with an energy, $h\nu_t$, less than half the bandgap and at moderate intensity is also used. It is not necessary for the experiments presented in figure 6 but gives the possibility of later comparison.) The higher energy raises the capacitance to a saturated value, the same for each V_1 and almost equal to a saturated value of the insulator capacitance, C_i , while this is not obtained for the lower energy before $t = t_{off}$.

When the light is switched off at $t = t_{loff}$ there is almost no decay after illumination with 1.7 eV while there is a small decay after illumination with 2.2 eV. The space charge region is very thin in our samples and sensitive to uncontrolled interface properties. The decay of the induced remaining change of the capacitance has not been studied further but in some samples with low leakage of the insulator it is about 50 % in 24 h.

Injected majority carriers reset the capacitance rather fast as can be seen from the curves at $t = t_{Voff}$. When the bias is on again the value of the capacitance becomes the same as before the illumination, which indicates that there is no excess charge left. If the cycle is repeated, good reproducibility is achieved.

The rate of the raise of the capacitance after t_{lon} should be the same for different V_1 if the excitation rate of charge carriers per unit area is constant. This can be seen in figure 6, where for each bias voltage V_1 the capacitance is recorded during illumination with light of identical intensity and energy. The photoionization cross section is dependant on the energy of the extrinsic light and therefore variations of the light energy will change the rate of excitation of charge carriers. The two different slopes corresponding to two different light energies (1.7 eV and 2.2 eV) can be seen (figure 6).

It is evident from the above experiments that charge carriers are accumulated and that this effect greatly influences the capacitance. It is then important to show how this excess charge affects the CV-curve in order to apply equation (1). The new population of the surface states might, for example, be more dependant on the change of bias. It is readily seen that if the device is depleted, and provided that $N_d - N_a$ in equation (9) is not changed by the illumination in the sensing layer of the testing signal from the capacitance meter, the only parameter which might be affected in equation (9) by illumination is the surface charge Q_{ss} . If therefore the CV-curve is recorded by a nonsaturating constant excess surface charge, ΔQ_{ss} , the CV-curve according to equations (9) and (6) should only be shifted along the voltage axis.

Figure 6 shows how an increase of the capacitance is obtained with illumination. Assuming this is caused by a excess surface charge, ΔQ_{ss} , the following experiments are done (figure 7). The CV-curve is first recorded in darkness, curve a, using a triangle sweep as earlier for the bias. At the next cycle the bias sweep is stopped at a constant value V_1 .

The device is now illuminated with the same light used for figure 6. Depending on the energies $h\nu_p + h\nu_t$, and illumination time, $t_{loff} - t_{lon}$, different values of the capacitance are obtained before t_{loff} , (figure 6). Some seconds after t_{loff} the bias sweep is continued and the cycle is completed (figure 7, curve c-c'-d respectively g-g'-f).

If the recorded curves c-c'-d and g-g'-f in figure 7 are shifted along the voltage axis they coincide with the curve a. The above assumptions can then be seen to be well verified for those parts, c-c' and d-d', of the curves which are obtained when the bias goes from V_1 to its maximum and back to V_1 . The parts of the curves, d and f, which are then recorded when the sweep continues from V_1 to zero are somewhat distorted and are slightly above the curve a. This can be explained by the increasing influence of uncontrolled interface properties and if the new value of $N_d - N_a$ in the region nearest the interface because of the illumination is much different from the value in the bulk this will also contribute.

The above experiments (figures 4-7) support the proposition that eq 1 still validly describes the CV-curve for a depleted MIS-structure when the device is illuminated with proper extrinsic light. The created minority carriers are accumulated as an excess surface charge, ΔQ_{ss} . The recombination and/or thermal generation in the space charge region is shown to be very low and a remaining constant surface charge, after the light is switched off, causes a constant shift, ΔV , along the voltage axis which can be expressed (equation 6) by

$$\Delta V = - \frac{\Delta Q_{ss}}{C_i} \quad \dots(14)$$

The shift may be estimated from the CV-curves (figure 7) and put into equation (12) to give information about the deep energy levels if proper light is used.

The correction factor (12) in equation (13) caused by the changing excitation volume (figure 2) must then be taken into account. To avoid this and to take advantage of a constant excitation volume the bias V_1 is controlled in order to keep W_s constant. With reference to figure 7 this means that the vertical curve b, which is recorded during illumination, will be horizontal. This is done by a feedback controlled amplifier which senses the value of the capacitance by the output signal of the capacitance bridge, originally set by the chosen bias and then gives the necessary bias, $V_1 + \Delta V$, for a constant capacitance during illumination. ΔV is then related to the created excess surface charge ΔQ_{ss} (equation 14). Equation (13) can now be reduced to

$$\Delta V' = \text{const} \cdot \sigma_{vt} \cdot I_t \cdot t \quad \dots(15)$$

for constant photonenergy, $h\nu_p$, and intensity, I_p , of the population controlling light source.

The straight lines described by equation (15) are verified experimentally (figure 8), where the bias $V_1 + \Delta V$ is recorded as a function of illumination time t in steady state. The upper curve is recorded without illumination and gives an indication on the thermal excitation and the stability of the experimental equipment. The next curve is recorded when the sample is illuminated with the population controlling light only (1.78 eV). The lowest three curves represent the case when light of different energies ($h\nu_t = 0,70, 0,90$ and $1,0$ eV respectively) are added to the controlling light. The intensity of this light was kept constant and high compared to the added light to allow the excitation by this not to be limited by a too high population in the level a (figure 3).

Keeping the intensity of the test light, I_t , constant the slopes of straight lines (figure 8) should be proportional to the photoionization cross section, σ_{vt} . In order to find the spectral distribution of the photoionization cross sections, a collection of curves similar to those in (figure 8) for different energies of the testing light were recorded and the slopes according to equation (15) were plotted as a function of $h\nu_t$ (figure 9).

The curve corresponds quite well to a Lucovsky plot (9) for 0,69 eV. Using methods earlier referred to (3, 4) on MIS-structures with a leaky insulator the same energy level was identified which is suggested to be a Cu-level. (In these leaky MIS-structures a more pronounced influence of a change of the factor $N_d - N_a$ was noticed since the screening effect due to accumulated minority carriers are here much less, because of the charge transportation through the insulator.)

Conclusion

A measurement method for studying deep levels in semiconductors is suggested and experimentally verified based on a principle using excess charge, due to light excitation in the space charge region of a MIS-structure, which is accumulated at the semiconductor surface and measured as a voltage shift of the CV-curve. This shift is measured with a feedback-controlled amplifier which keeps the space charge region constant during the excitation by increasing the set gate voltage.

A factor proportional to the photoionization crosssection for excitation to a deep lying acceptor level is deduced. MIS-structures in GaP are made which fit the model well and an acceptor level at about 0,7 eV from the valence band, probably due to Cu levels, is found.

It should be possible to use the studied MIS-structures in similar ways as light sensitive charge coupled devices, and they may have advantages due to the stronger depletion mode and low recombination which give a long life memory effect. A space charge memory effect might have been more pronounced if an n-type semiconductor material with a deep level in the upper half of the forbidden gap had been used, since excitation of minority carriers then could be avoided.

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References

- 1 A S Grove, B E Deal, E H Snow and C T Sah
Investigation of Thermally oxidized silicon surfaces using
metal-oxide-semiconductor structure
Sol Stat El 8 pp 145 - 163 Feb 65.

- 2 W S Boyle and G E Smith
Charge coupled semiconductor devices
The Bell Syst T J Ap 70 p 587

- 3 H G Grimmeiss and G Olofsson
Charge-carrier capture and its effect on transition
capacitance in GaP-Cu diodes
J Applied Physics 40 no 6 May 69

- 4 G Björklund and H G Grimmeiss
Determination of optical cross sections in GaP using
charge storage and impurity photovoltaic effect
Sol Stat El pp 589 - 601 (71)

- 5 S Braun and H G Grimmeiss
Thermal and optical generation in reverse-biased gold-doped
silicon p^+n junctions without the depletion approximation
J Applied Physics 44 No 6 June 73 p 2789

- 6 B Goldstein and S S Perlman
Electrical and Optical properties of highresistivity Gallium
phosphide
Phys Rev 148 no 2 Aug 66 p 715

- 7 A M Goodman
Metal-semiconductor barrier height measurement by the
differential capacitance method - one carrier system
J Appl Physics 34 no 2 Feb 63

- 8 J Grosvalet and G Jund
Influence of illumination on MIS capacitors in the strong
inversion region
IEEE Trans Electron Dev ED-14 pp 777-780 (Nov 67)

- 9 G Lucovsky
On the photoionization of deep impurity centers in semi-
conductors
Sol State Comm 3 p 299 (65)

Figure captions

- fig 1 Schematic representation of an MIS capacitor and how it is illuminated.
- fig 2 Energy level diagram of a metal-insulator n-type semiconductor combination.
 a) When a voltage V has just been applied to the metal electrode.
 b) After the accumulation of some positive carriers (optically or thermally excited) at the insulator-semiconductor interface.
- fig 3 Carrier generation through a deep acceptor level with binding energy E_a when simultaneously illuminated with extrinsic photons of different energy $h\nu_p$ and $h\nu_t$ the intensities of which are I_p and I_t respectively.
- fig 4 MIS capacitance recorded vs gate voltage. Arrows indicate the triangle sweep (0,05 Hz) direction.
 a without optical excitation
 b-c low optical excitation
 d-e medium optical excitation
 f-g strong optical excitation
- fig 5 Normalized MIS capacitance vs gate voltage.
- fig 6 MIS capacitance recorded vs time with optical excitation $h\nu_p$ and bias, V_1 , as indicated $h\nu_t = 0,8$ eV.
- fig 7 MIS capacitance recorded vs gate voltage. Arrows indicate the triangle sweep (0.05 Hz) direction. The sweep is stopped at $V = V_1$ for optical excitation with $h\nu_p = 1.78$ eV + $h\nu_t = 0,8$ eV in 20 seconds. The intensity I_t of the test light, $h\nu_t$, is constant. The intensity, I_p , of the controlling light, $h\nu_p$, is set at two different values corresponding to curves b and b' with the highest intensity for the b' curve.
- fig 8 The gate voltage $V_1 + \Delta V$ recorded vs time. $V_1 = -4$ volts. The upper curve without optical excitation. The lower curves with optical excitation as indicated.
- fig 9 Comparison of Lucovsky's theory (9) (-) with the spectral dependance of the photoionization cross section $\sigma_{vt} \cdot \text{const}$ for the excitation of electrons into an acceptor level in GaP (ooo).

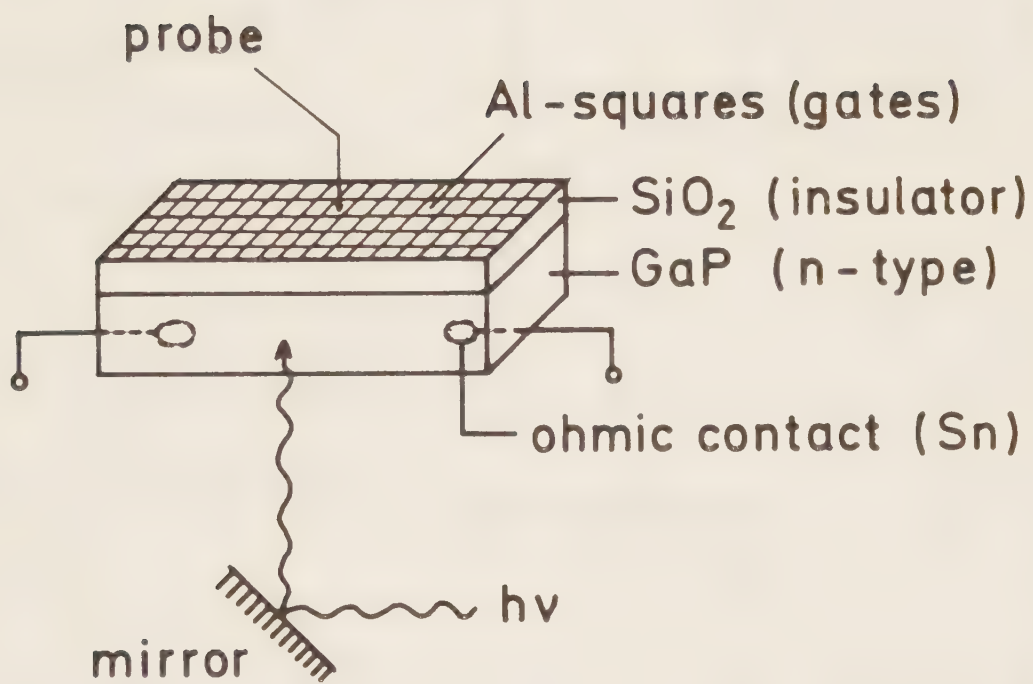
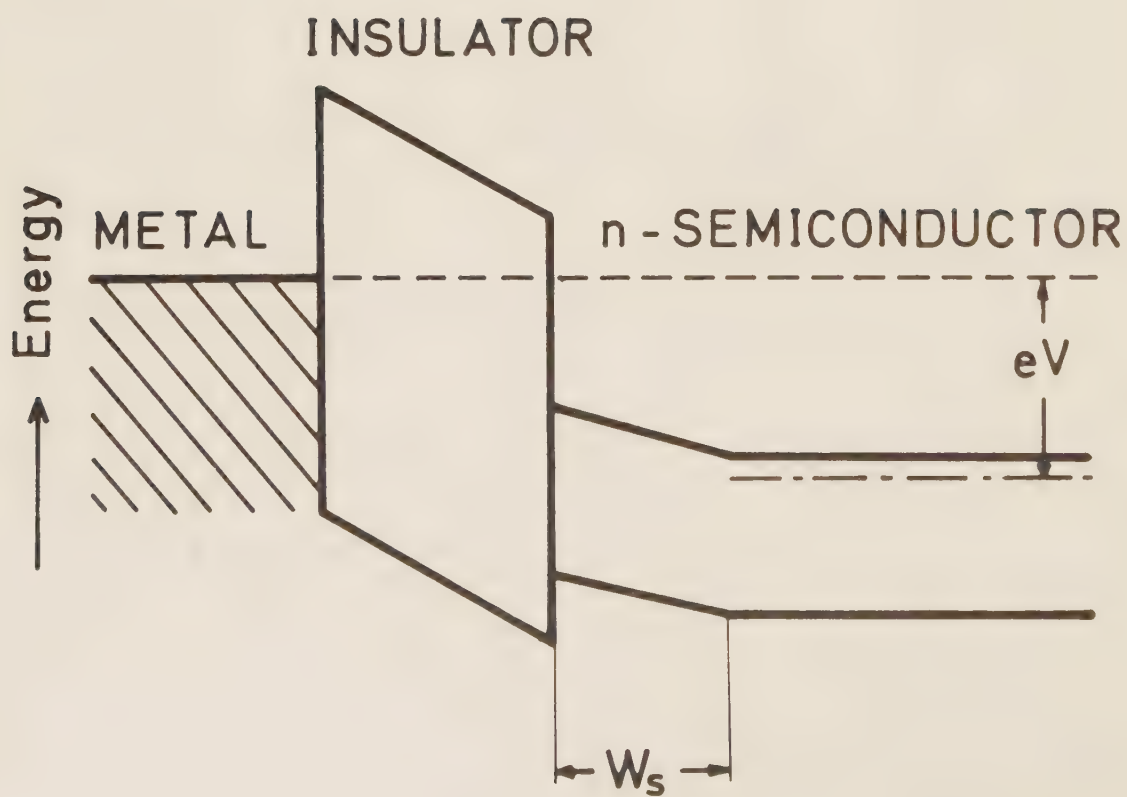
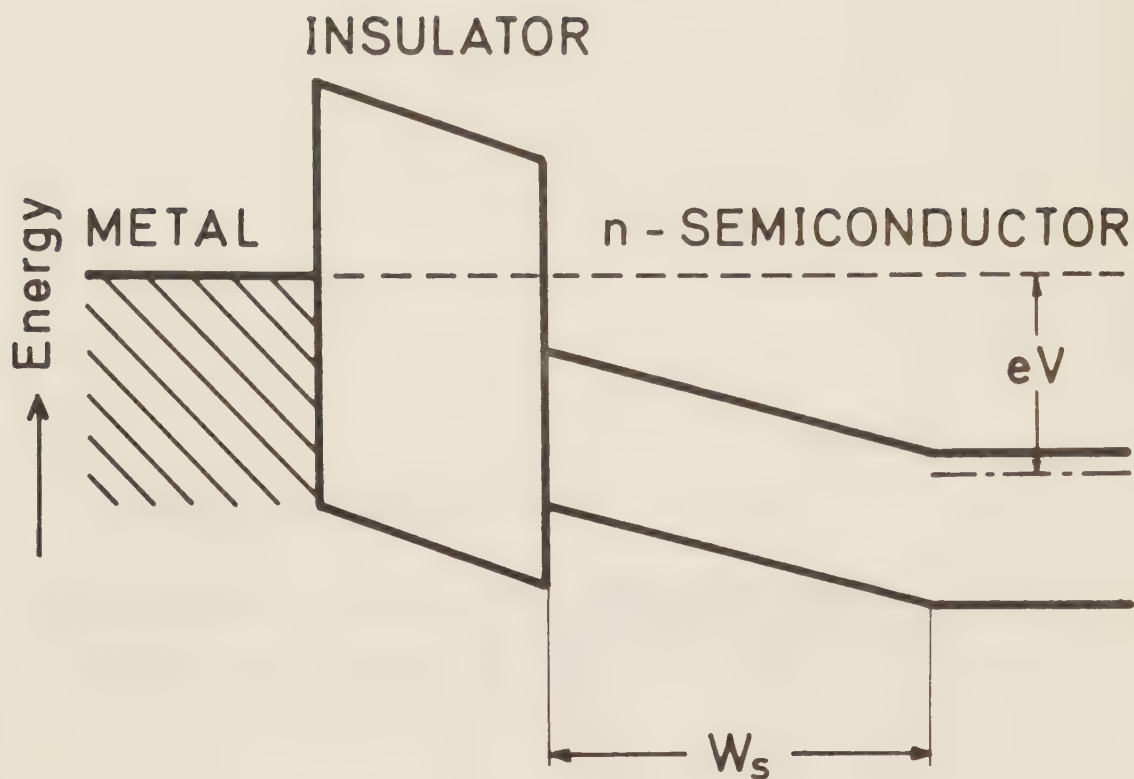


Fig 1



distance

Fig 2

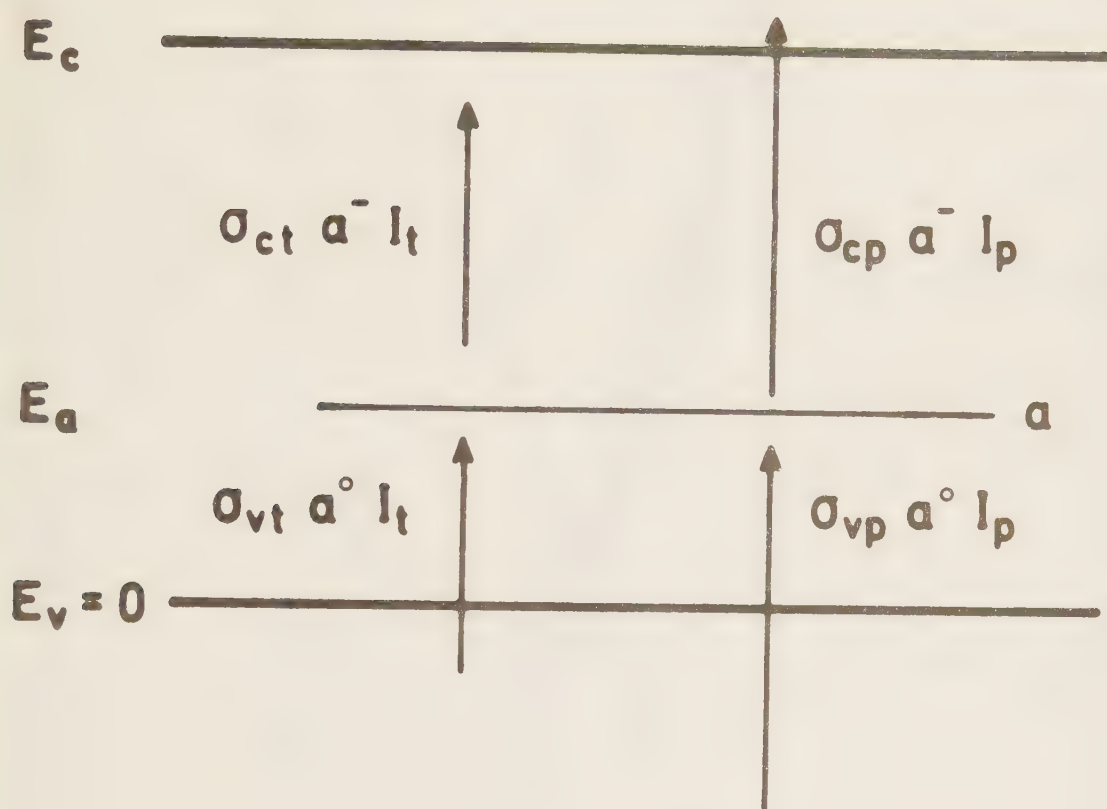


Fig 3

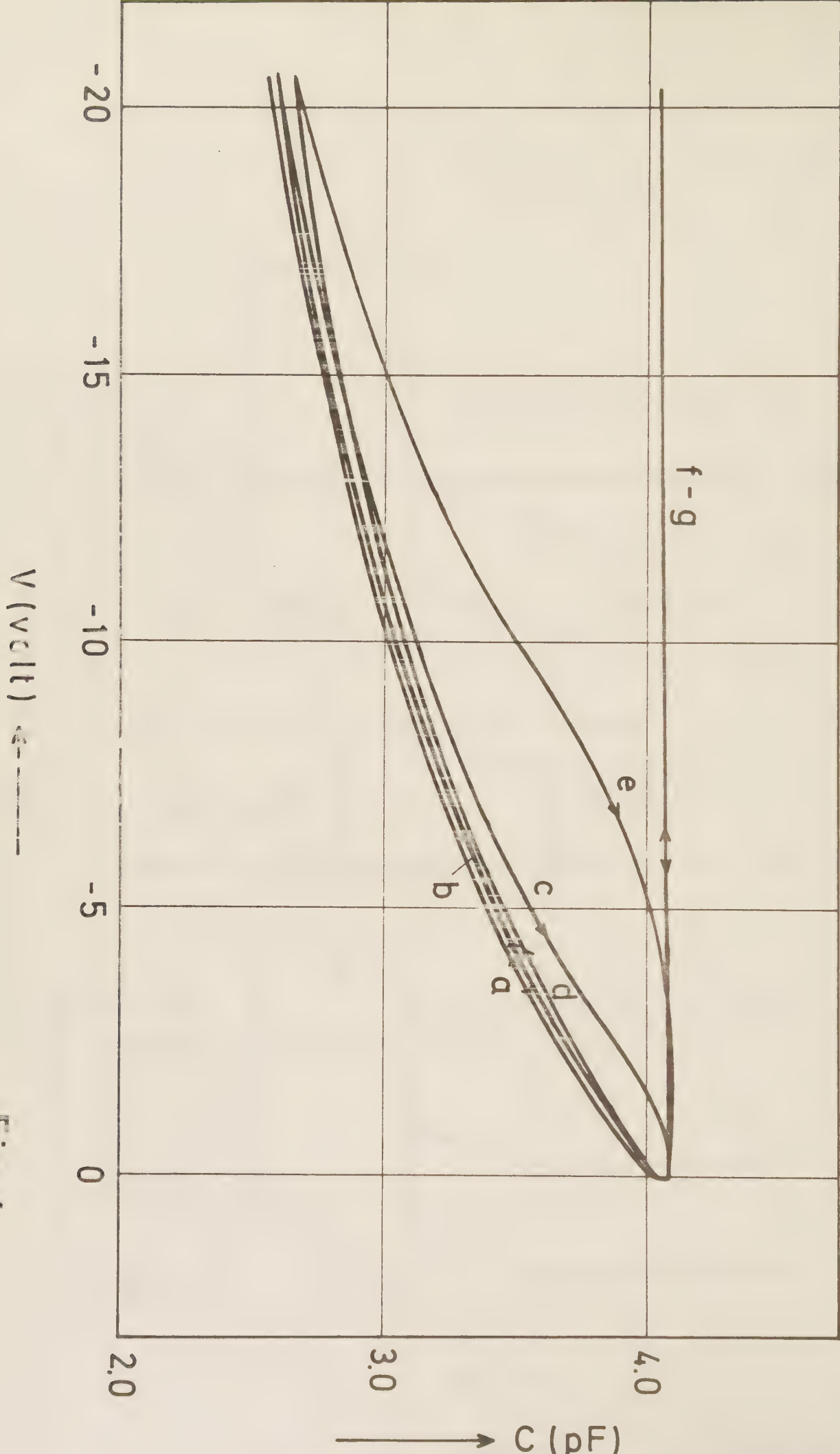


Fig 4

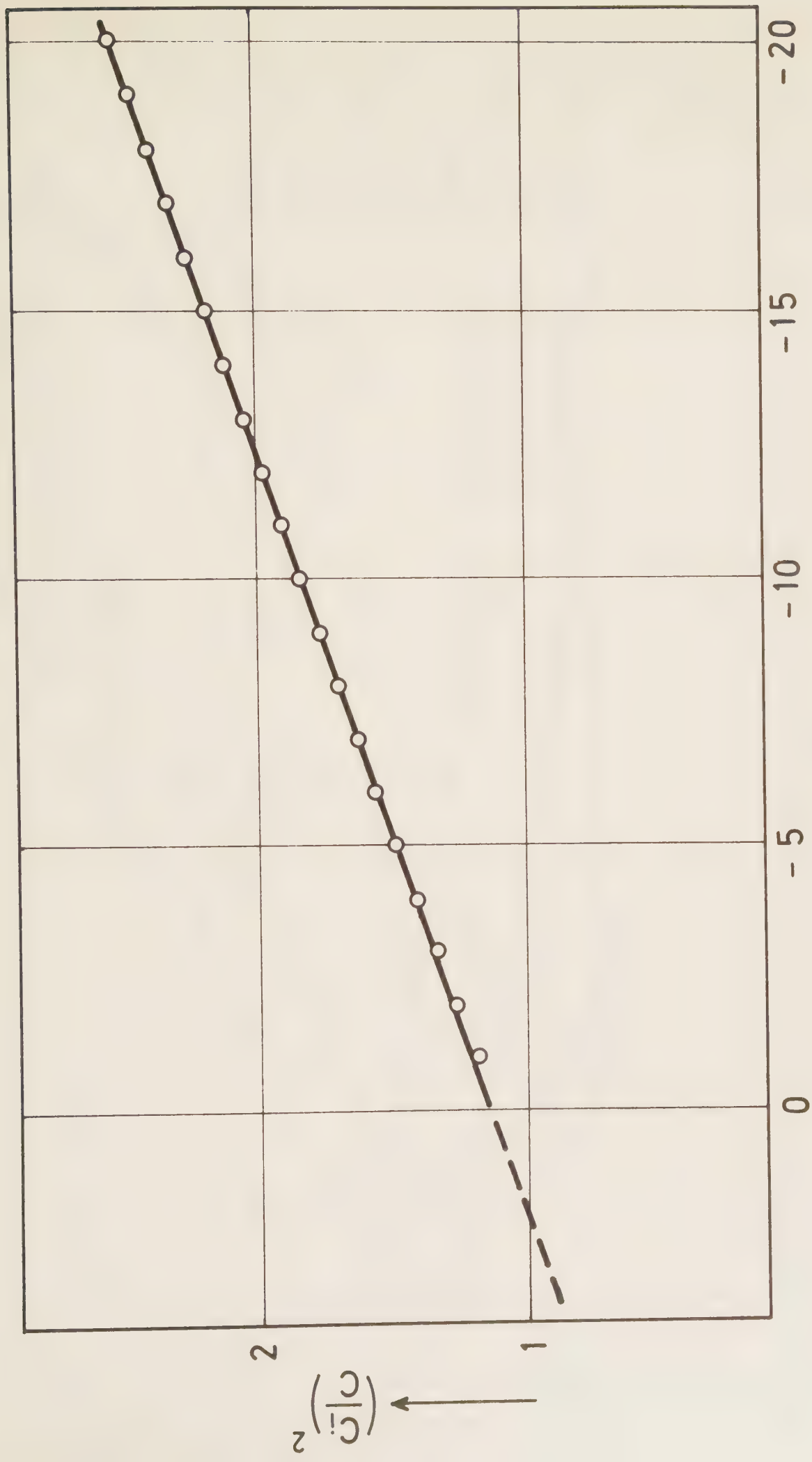


Fig 5

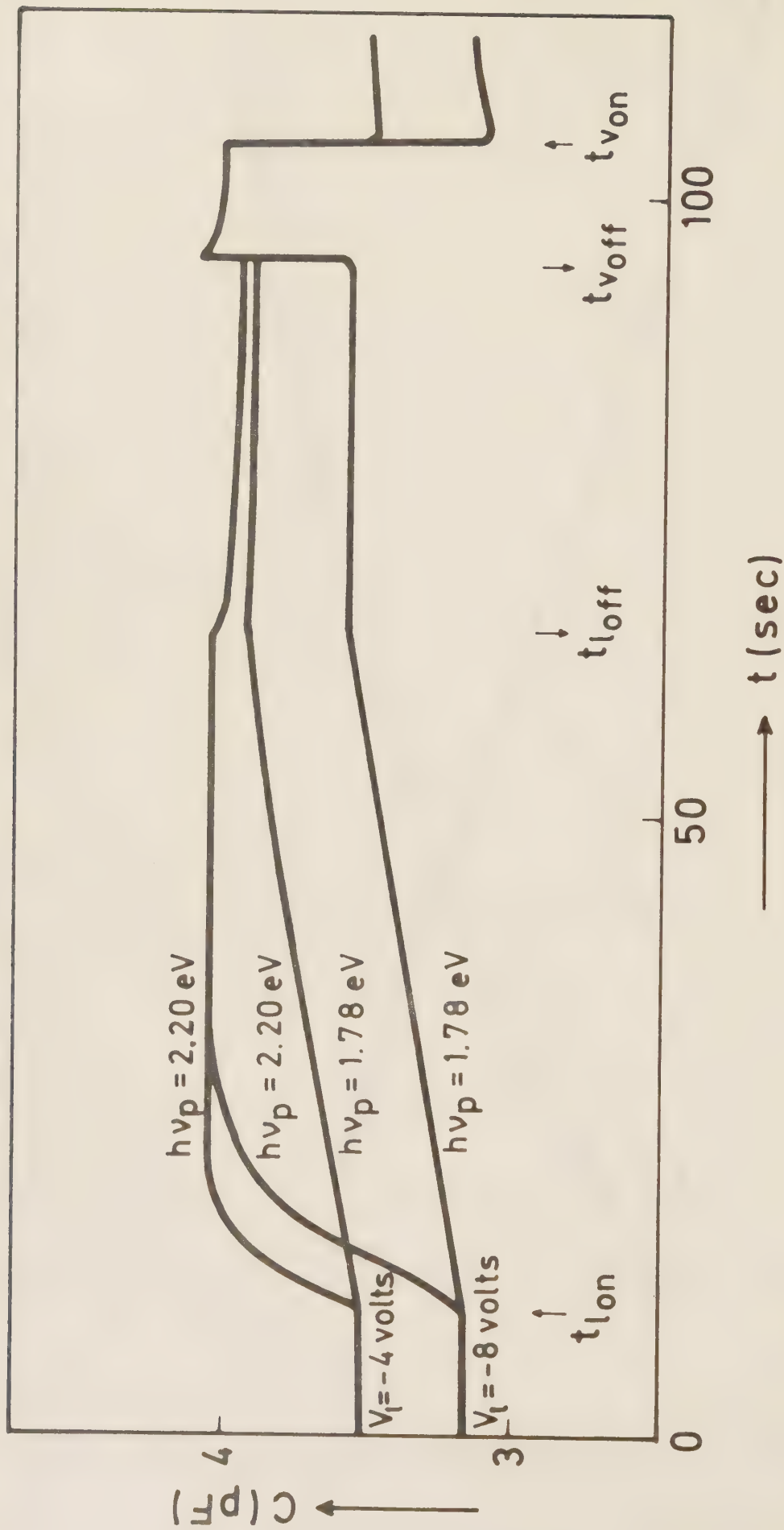


Fig 6

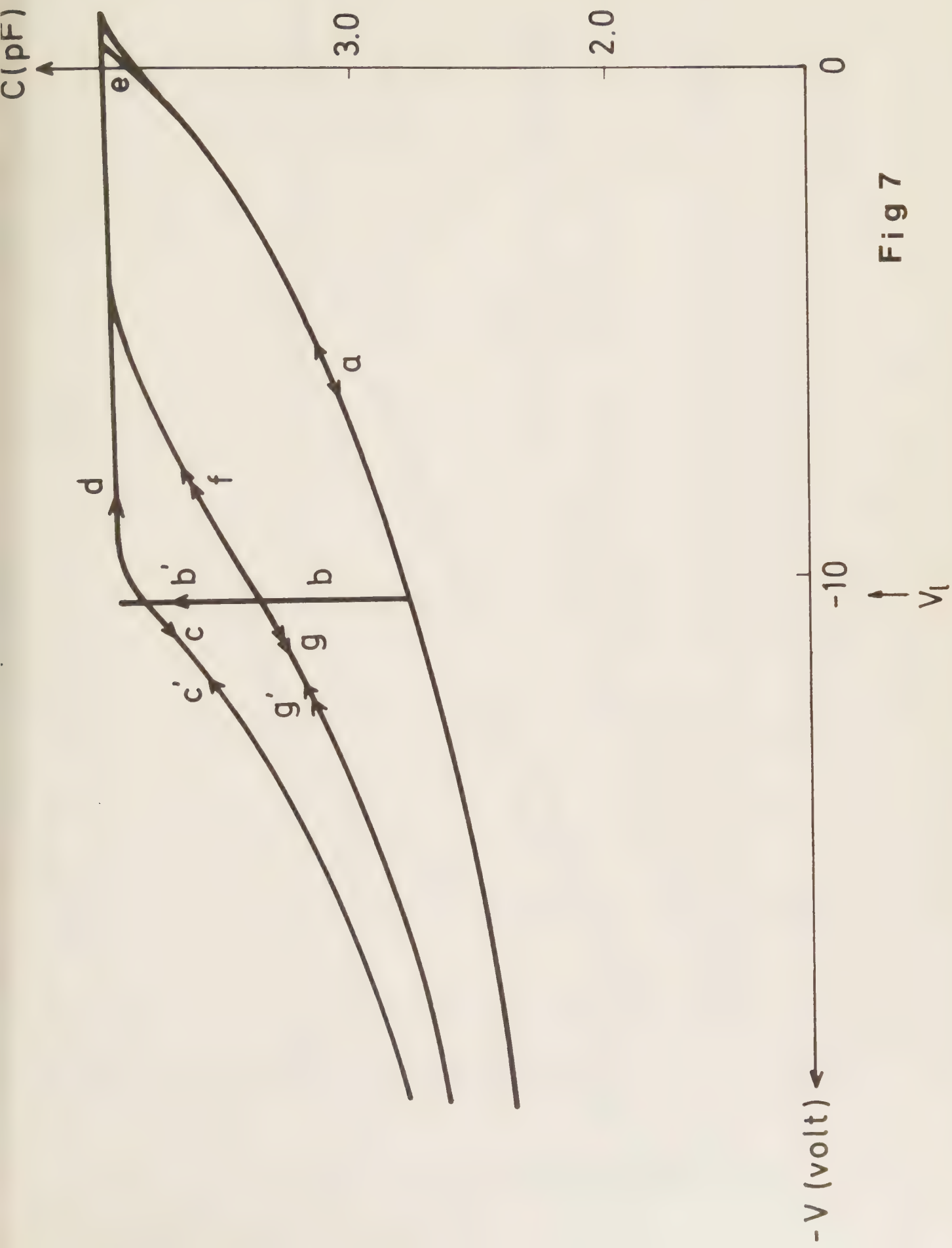
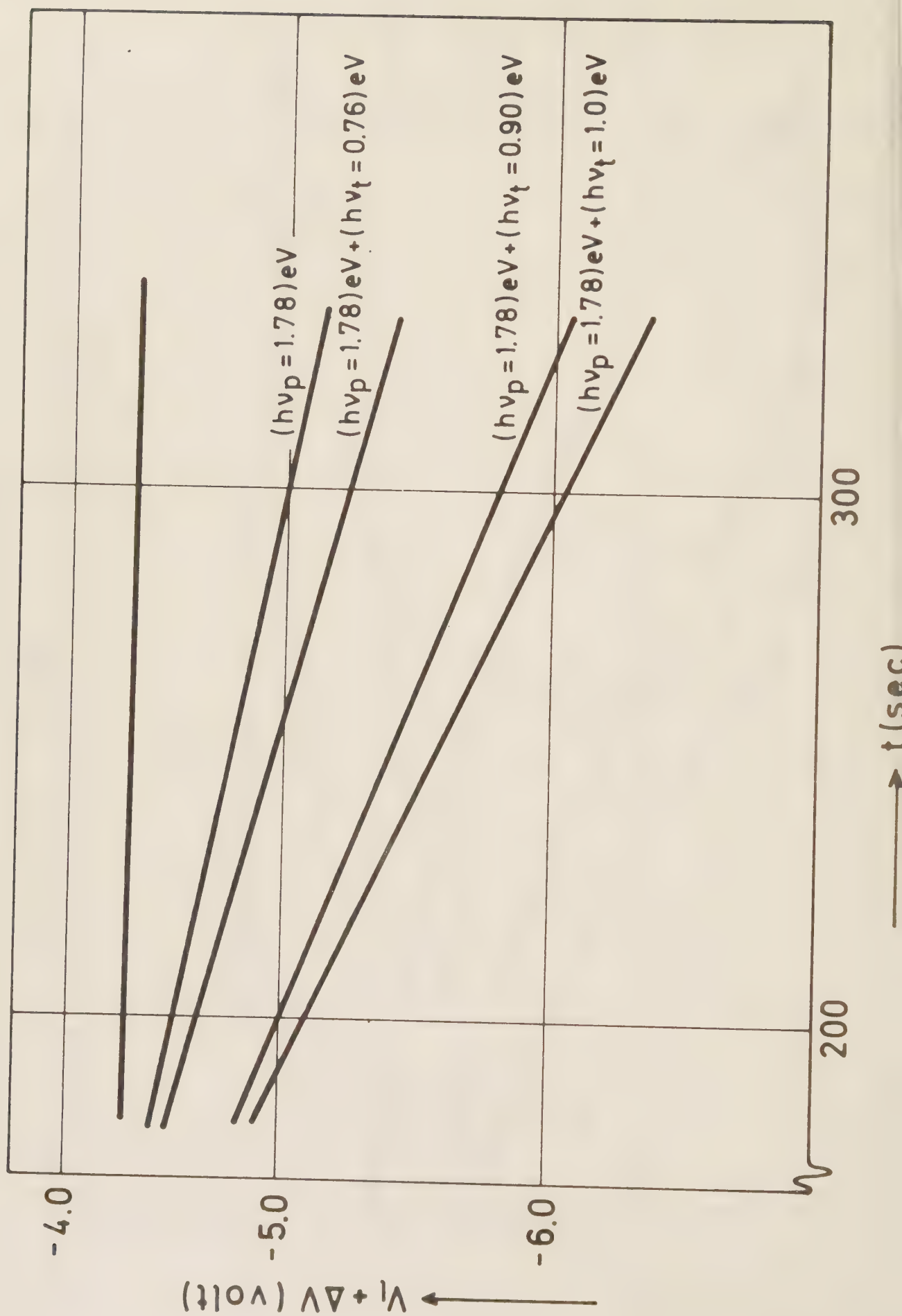


Fig 7



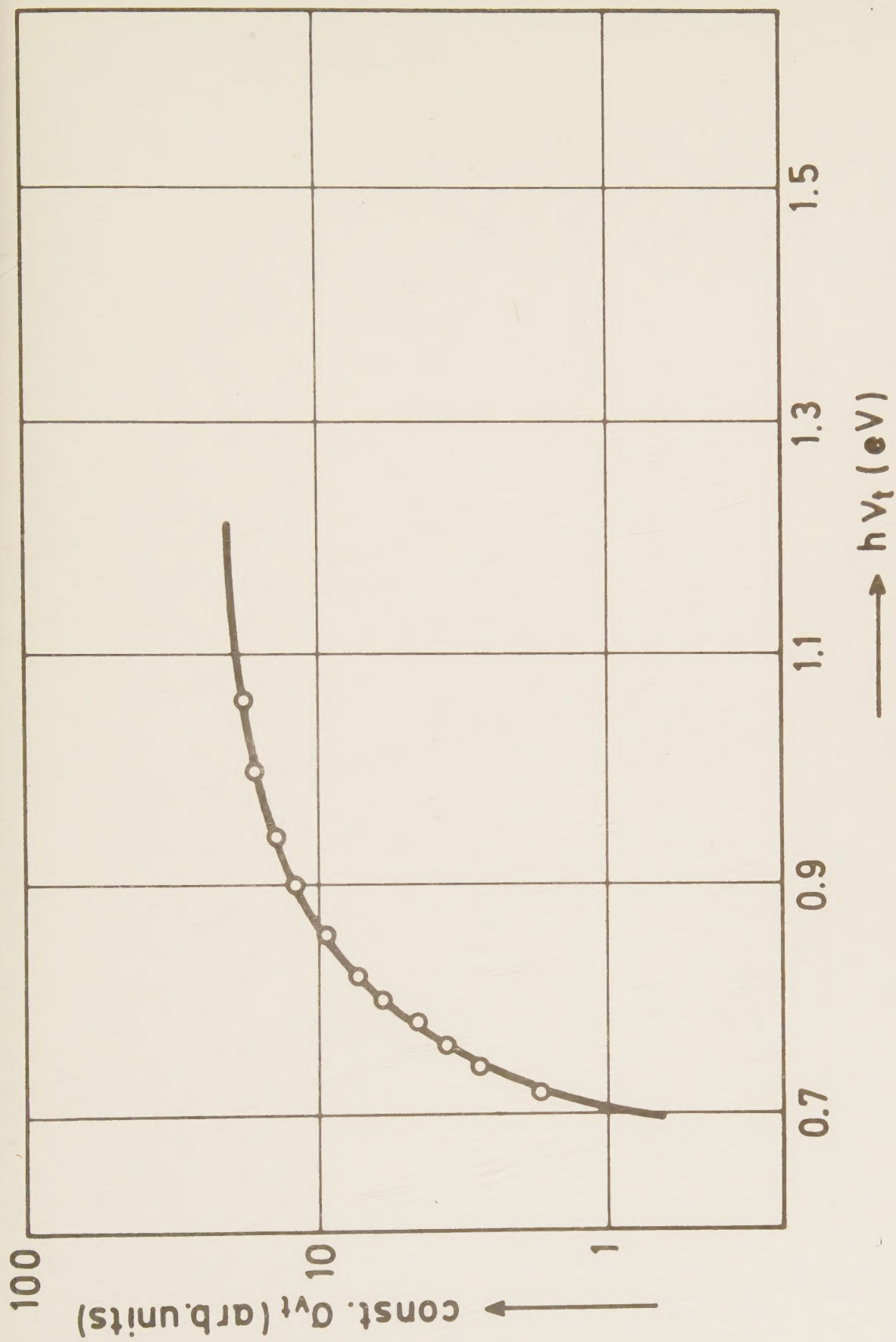


Fig 9

